Docket No. 2003US310

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re the application of:

Medhat A. TOUKHY et al.   Art Unit: 1752

Serial No. 10/677,318, filed October 3, 2003   Examiner: SCHILLING, Richard L.

For: **BOTTOM ANTIREFLECTIVE COATINGS**

ON APPEAL FROM THE PRIMARY EXAMINER TO THE BOARD OF PATENT APPEALS AND INTERFERENCES

APPELLANTS' BRIEF UNDER 37 C.F.R. § 41.67

March 26, 2008

Mail Stop Appeal Brief-Patents   **Attached:**
Commissioner for Patents
P.O. Box 1450
Alexandria, Virginia 22313-1450

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Serial No. 10/677,318
Filed: October 3, 2003
Appellant's Brief under 37 C.F.R. § 41.67

Dear Sir:

The present Appeal Brief is submitted in support of the Notice of Appeal filed on February 8, 2008, and received on February 8, 2008, by the United States Patent and Trademark Office.

REAL PARTY IN INTEREST

The real party in interest is AZ Electronic Materials USA Corp.

RELATED APPEALS AND INTERFERENCES

There are no related appeals or interferences.

STATUS OF CLAIMS

Claims 1 to 9 and 32 to 37 are pending in the present application, stand rejected and are the subject of this appeal. Claims 16 to 31 and 38 to 46 had been previously withdrawn but they have been canceled and are now the subject of pending divisional application, serial no. 11/873,522, filed October 17, 2007.

STATUS OF AMENDMENTS AFTER FINAL REJECTION

No amendments have been made subsequent to the final Office Action dated November 8, 2007

SUMMARY OF CLAIMED SUBJECT MATTER

Appellants' invention is for an antireflective coating composition that contains a base that is not soluble in a solvent of a photoresist composition.

Claim 1 provides an antireflective coating composition useful with a photoresist composition. According to claim 1, an antireflective coating composition (page 3, line 28 to page 4, line 8; page 11, line 15 to page 12, line 11) has at least one base which is not soluble in a solvent of the photoresist composition (page 8, line 14 to page 11, line 13). Appellants show that an antireflective coating composition that contains a base that is not soluble in the solvent of a photoresist composition has better performance than an antireflective coating composition that contains a base that is soluble in the solvent of a photoresist composition (page 12, line 15 to page 14, line 5).

This summary does not provide an exhaustive or exclusive view of the present subject matter and Appellants refer to the appended claims and their legal equivalents for a complete statement of the invention.

GROUNDS OF REJECTION TO BE REVIEWED

In the final Office Action, claims 1 to 9 and 32 to 37 were rejected under 35 U.S.C. § 112, first paragraph. Claims 1 to 9 and 32 to 37 were rejected under 35 U.S.C. § 102(b) as being fully met by Hasegawa et al. (US 6280898) or Sato et al. (US 2002/0098440). Claims 1 to 9 and 32 to 37 were rejected under 35 U.S.C. § 102(e) as being fully met by Nishimura et al. (US 6800414).

ARGUMENT

Rejection of claims 1 to 9 and 32 to 37 under 35 U.S.C. § 112, first paragraph

When rejecting a claim under the enablement requirement of 35 U.S.C. §112, the Patent Office bears an initial burden of setting forth a reasonable explanation as to why it believes that the scope of protection provided by that claim is not adequately enabled by the description of the invention provided in the specification. *In re Wright*, 999 F.2d 1557, 1561-62, 27 USPQ2d 1510, 1513 (Fed. Cir. 1993).

This includes, of course, providing sufficient evidence or scientific reasons for doubting any assertions or objective truths in the specification as to the scope of enablement. The first paragraph of 35 U.S.C. § 112 requires nothing more than an objective enablement. How such teaching is set forth, either by use of illustrative examples or by broad terminology, is irrelevant. *In re Marzocchi*, 439 F.2d 220, 223-24, 169 USPQ 367, 369-70 (CCPA 1971), *In re Wright*, 999 F.2d at 1561, 27 USPQ2d at 1513.

A specification disclosure which contains a teaching of the manner and process of making and using the invention in terms which correspond in scope to those used in describing and defining the subject matter sought to be patented must be taken as in compliance with the enabling requirement of the first paragraph of 35 U.S.C. § 112 unless there is reason to doubt the objective truth of the statements contained therein which must be relied on for enabling support. Furthermore, it is incumbent upon the Patent Office, whenever a rejection under the first paragraph of 35 U.S.C. § 112 is made, to explain why it doubts the truth or accuracy of any statement in a supporting disclosure and to back up those assertions with acceptable evidence or scientific reasoning which is inconsistent with

the contested statement and clearly and fully explain why one of ordinary skill in the art would not have been able to make and use the full scope of the subject matter claimed based on the written description of the invention in the specification without undue experimentation. *Marzocchi, id.* Otherwise, there would be no need for appellants to go to the trouble and expense of supporting their presumptively accurate disclosure. The Patent Office has failed to adequately explain or support why it doubts the truth or accuracy of any statement in appellants' disclosure and to back up those assertions with acceptable evidence or reasoning which is inconsistent with appellants' disclosure.

The Patent Office has not provided any evidence or scientific reasoning to support its allegation that appellants' claims 1 to 9 and 32 to 37 are not enabled. All the Patent Office has stated is that "the specification, while being enabling for polymer containing antireflection layers, does not reasonably provide enablement for antireflection layers with only basic compounds. Polymers are necessary as binders for the layers to bind the basic compounds and as radiation absorbers for antireflection or as binders for radiation absorbers."[1] In a later Office Action, the Patent Office stated that "[t]he claims include compositions without the polymers and/or absorbers which are essential components."[2]

The Patent Office has not met its burden of setting forth a reasonable explanation as to why it believes that the scope of protection provided by the claims is not adequately enabled by the description of the invention as provided for in the specification since it not provided any evidence or scientific reasoning that doubts any assertions or objective truths in appellants' specification. *Marzocchi, id.*

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[1] See Office Action dated July 12, 2006, page 3, paragraph 5.
[2] See final Office Action dated November 20, 2006, top of page 3.

Appellants' specification provides materials and the process for making and using the antireflective coating compositions (specification, page 3, line 28 to page 4, line 8; page 7, lines 4 to 15; page 11, line 15 to page 12, line 11; page 12, line 15 to page 14, line 5). Since appellants' specification contains a written description of the suitable materials and the process for making and using the antireflective coating compositions corresponding with the scope of the pending claims, compliance with the enablement requirement is presumed. Sufficient disclosure can be achieved through illustrative examples as well as terminology to teach those of ordinary skill in the art how to make and use appellants' invention as broadly as it is claimed. *In re Vaeck*, 947 F.2d 488, 496 & n. 23, 20 USPQ2d 1438, 1445 & n. 23 (Fed. Cir. 1991) ("The first paragraph of § 112 requires nothing more than *objective* enablement. *In re Marzocchi,* 439 F.2d 220, 223, 169 USPQ 367, 369 (CCPA 1971). How such a teaching is set forth, either by the use of illustrative examples or by broad terminology, is irrelevant. *Id.*"(emphasis in original)).

Appellants provide illustrative examples to show and teach a person having ordinary skill in the art how to make and use their invention. See page 10, line 19 to page 11, line 13 and page 12, line 15 to page 14, line 5 of appellants' specification.

The Patent Office has failed to explain why appellants' specification would not have been suitable for a person of ordinary skill in the art to practice the full scope of the claimed subject matter. The Patent Office has simply concluded that the specification is not sufficient to support the claimed invention without any factual evidence or scientific evidence to support its position.

The Patent Office stated that the "specification fails to disclose how to use a composition only containing one of the recited base compounds as encompassed by the

instant claims."[3] This is just a conclusion without sufficient evidence or any scientific reasoning provided to support such a conclusion. The Patent Office fails to take into account that appellants' composition is an antireflective coating composition, which is clearly understood by the skilled artisan and to which appellants have provided sufficient information thereto (see, for example, page 4, lines 1 to 8 and page 12, line 15 to page 14, line 5 of appellants' specification).

Whether a claimed invention is enabled is not a single, simple factual determination, but rather is a conclusion reached by weighing many factual considerations. To assist the Patent Office in meeting its initial burden in making a 35 U.S.C. § 112, first paragraph, rejection, a number of factors that should be considered are set forth in MPEP §2164.01(a). The factors to be considered in determining whether a claimed invention is enabled throughout its scope without undue experimentation include the quantity of experimentation necessary, the amount of direction or guidance presented, the presence or absence of working examples, the nature of the invention, the state of the prior art, the relative skill of those in the art, the predictability or unpredictability of the art, and the breadth of the claims.

The Patent Office has provided no analysis of these factors. In fact, the Patent Office has not set forth a reasonable explanation as to why it believes that the scope of appellants' claims is not adequately enabled by appellants' specification. Instead, the Patent Office's only provides unsupported conclusions as to why the specification does not enable the claimed invention.

For example, the Patent Office stated that the specification failed to disclose how to use and coat compositions as encompassed by the instant claims without polymers and

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[3] See final Office Action dated November 8, 2007, page 2, paragraph 1.

absorbers.[4] Appellants' compositions are antireflective coating compositions which are know to those persons skilled in the art as containing polymers and absorbers. Appellants have demonstrated that their antireflective coating composition contains polymers and absorbers as shown in their examples on page 12, line 15 to page 14, line 5 of their specification. The Patent Office appears to be of the opinion that that any knowledge in the prior art needed to establish enablement must be recited in the specification. This is not correct. It has been well established that "[a] patent need not teach, and preferably omits, what is well known in the art. *Hybritech*, 802 F.2d at 1384, 1384, 231 USPQ at 94." *Spectra-Physics, Inc. v. Coherent, Inc.*, 827 F.2d 1524, 1534, 3 USPQ2d 1737, 1743 (Fed. Cir. 1987), *cert. denied*, 484 U.S. 954 (1987). Stated another way, a patent appellant need not include in the specification that which is already known to and available to the public. *Paperless Accounting, Inc. v. Bay Area Rapid Transit Sys.*, 804 F.2d 659, 664, 231 USPQ 649, 653 (Fed. Cir. 1986).

The test of enablement is whether one reasonably skilled in the art could make or use the invention from the disclosures in the patent coupled with information known in the art without undue experimentation. *U.S. v. Telectronics, Inc.*, 857 F.2d 778, 785, 8 USPQ2d 1217, 1223 (Fed. Cir. 1988) (citing *Hybritech Inc. v. Monoclonal Antibodies, Inc.*, 802 F.2d 1367, 1384, 231 USPQ 81, 94 (Fed. Cir. 1986)). Determining what the specification fails to explicitly set forth is, at best, only a first step in demonstrating that a disclosure is not enabling.

The Patent Office has also failed to consider and appreciate that appellants have shown that antireflective coating compositions are well known to those persons having ordinary skill in the art. The term antireflective coating composition in itself contains polymers, binders and other components that make it work. This is clearly understood by

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[4] See Office Action dated August 1, 2007.

the skilled artisan. Appellants have demonstrated, by illustrative examples, what is an antireflective coating composition as well as how to use and coat antireflective coating compositions of the present invention (see page 10, line 19 to page 11, line 13 and page 12, line 15 to page 14, line 5 of appellants' specification). Appellants have also incorporated by reference, as discussed below, documents that provide sufficient information, of which the skilled artisan is well aware, on antireflective coating compositions (see page 3, line 28 to page 4, line 8 of appellants' specification). Appellants' invention is to take antireflective coating compositions and add bases that are not soluble in solvent of a photoresist composition.

The Patent Office is complaining that the full description of antireflective coating composition does not contain polymers and absorbers. That is incorrect. "It is well settled that the disclosure of an application embraces not only what is expressly set forth in words or drawings, but what would be understood by persons skilled in the art. As was stated in *Webster Loom Co. v. Higgins et al.*, 105 U.S. 580, 586 (1881), the appellant 'may begin at the point where his invention begins, and describe what it has made that is new and what it replaces of the old. That which is common and well known is as if it were written out in the patent and delineated in the drawings.'" *In re Howarth*, 654 F.2d 103, 106, 210 USPQ 689, 692 (CCPA 1981). It is certainly appropriate to refer to incorporated material, which is clearly a part of the written description itself. See *Chiron Corporation v. SourceCF Inc.*, 431 F.Supp. 2d 1019, 1031-1032, n. 5 (N.D. Cal. 2006). Those components that make up antireflective coating compositions are well known to the skilled artisan. This is clearly demonstrated in appellants' specification at page 11, line 15 to page 12, line 11 and at page 12, line 15 to page 14, line 5. Appellants have gone further by incorporating by reference sufficient material that demonstrate antireflective coating compositions. See page 3, line 28 to page 4, line 8 of appellants' specification. This is a clearly recognized procedure to meet the disclosure requirements of 35 U.S.C. § 112. See *Howarth*, 654 F.2d at 106, 210 USPQ at 692.

From the documents incorporated by reference in appellants' specification at page 4, lines 1 to 8, it is clear that antireflection coating compositions are well known to the skilled artisan[5]:

The ARCs of the invention in general comprise a crosslinker and a resin binder that effectively absorbs deep Uw [*sic*.] exposure radiation to reduce reflections of same. **From US 5886102, column 3, lines 39 to 42**

To prevent reflection of activating radiation into a photoresist coating, it is known to provide antireflective layers (ARC's) between a substrate and a photoresist layer. These antireflective layers typically comprise an adsorbing dye dispersed in a polymer binder though some polymers contain sufficient chromophores whereby a dye is not required. When used, the dye is selected to adsorb and attenuate radiation at that wavelength used to expose the photoresist layer thus reducing the incidence of radiation reflected back into the photoresist layer. **From US 5635333, column 1, lines 43 to 52**

Antireflective coating compositions and their uses are also known in the art and are described in numerous articles such as in the IEEE Transactions on Electron Devices, Edition 28, No. 11 of November 1981, pp. 1405-1410, entitled "Line Width Control and Projection Lithography Using a Multi-Layer Resist Process" by O'Toole et al.; in "Reduction of the Standing Wave Effect in Positive Photoresist," Brewer et al, in the Journal of Applied Photographic Engineering, Vol. 7, No. 6, December 1981, pp. 184-186; in "Control of One-Micron Lines in Integrated Circuits," Carlson et al, Kodak, 80 Interface, October 1980, pp 109-113; and in U.S. Pat. Nos. 4,370,403; 4,668,166; 4,719,166; 4,828,960; 4,910,122; and 5,234,990, each incorporated herein by reference.

Typical antireflective coatings comprise an adsorbing dye dispersed in a suitable polymer binder in an amount sufficient to attenuate the reflection of activating radiation into a photoresist coating. In some formulations, the resin binder contains sufficient chromophores to enable adsorption of activating radiation without the use of a separate dye. Typically, when a dye is added, it is used in an amount of about

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[5] The Patent Office was directed to this portion of appellants' specification in its responses of January 29, 2007, June 14, 2007, and October 29, 2007.

0.1 to 10 grams per liter of coating composition and more preferably, in an amount of from 1 to 3 grams per liter of coating composition. In selection of the dye, care should be exercised to assure that the dye is compatible with the photoresist used and is thermally stable at processing temperatures used. Further, the dye should be non-volatile at the temperature used and must adsorb reflective radiation at the radiation wavelength used to expose the photoresist. Among the dyes which may be used are 2-(P-(dimethylamino)phenylazo) benzoic acid (Methyl red), 4-(phenylazo)resorcinol (Sudan orange) and di-n-butyl-(5-di-n-butylamino-2,4-pentadienylidene)-ammonium perchlorate. Polymers that may be used with or without dyes include aromatic urea sulfone and aromatic sulfone polymers. **From US 5702611, column 3, line 53 to column 4, line 19**

The present invention provides an antihalation composition suitable for use with a photoresist, the antihalation composition in general comprising a resin binder and a compound capable of causing a thermally induced crosslinking reaction of the resin binder. Components of the antihalation composition preferably can crosslink with an overcoated layer of the photoresist composition, thereby increasing adhesion between the two coating layers and avoiding notable problems of at least some prior antireflective systems. The antihalation compositions of the invention may further comprise an acid or acid generator compound to catalyze the reaction between the resin binder and the crosslinking compound, enabling the crosslinking reaction to proceed at relatively lower temperatures. As used herein, the term acid generator refers to a compound that generates an acid upon appropriate treatment of the compound, for example, upon exposure to activating radiation or thermal treatment. The thermally active crosslinker can be a variety of materials and, preferably, is an amine-based material such as a benzoguanamine-based or melamine-based resin. To enhance radiation absorption properties, the antihalation compositions of the invention may further include one or more dye compounds that absorb radiation at or near the exposure wavelength of the overcoated photoresist. **From US 5851738, column 2, line 65 to column 3, line 21**

Additional citations are also found at

US 5939236, column 3, line 13 to column 5, line 15

US 6277750, column 6, line 20 to column 7, line 30

US 6399686, column 3, line 52 to column 5, line 52

US 6503689, column 13, line 50 to column 16, line 26

Copies of the aforementioned US Patents are attached as APPENDIX 4.

While the specification must enable the skilled artisan to practice the full scope of the claimed subject matter, the specification need not necessarily describe how to make and use every possible variant of the claimed invention, for the artisan's knowledge of the prior art and routine experimentation can often fill gaps, interpolate between embodiments, and perhaps even extrapolate beyond the disclosed embodiments. "This Court has repeatedly explained that a patent appellant does not need to include in the specification that which is already known to and available to one of ordinary skill in the art. An inventor need not, however, explain every detail since he is speaking to those skilled in the art. We thus have noted that not every last detail is to be described, else patent specifications would turn into production specifications, which they were never intended to be." *Koito Mfg. Co., Ltd. v. Turn-Key-Tech, LLC*, 381 F.3d 1142, 1156, 72 USPQ2d 1190, 1200 (Fed. Cir. 2004) (citations omitted; internal quotes omitted).

Appellants' specification provides that antireflective coating compositions are well known in the art. A person skilled in the pertinent art would know how to make and use appellants' claimed invention: an antireflective coating composition containing a base which is not soluble in a solvent of a photoresist composition used with the antireflective coating composition. One skilled in the art would have sufficient knowledge in the background and the makeup of antireflective coating compositions as appellants have provided in their specification. The Patent Office has not demonstrated by factual evidence or scientific reasoning anything to the contrary.

Appellants' invention is that an antireflective coating composition has a base which is not soluble in a solvent of a photoresist composition used with the antireflective coating composition. The phrase antireflective coating composition has been clearly explained in appellants' application and is clearly understood by the skilled artisan. See, for example,

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page 3, line 28 to page 4, line 8; page 7, lines 4 to 15; page 11, line 15 to page 12 line 11; and page 12, line 15 to page 14, line 5. There is clear support for appellants' use of antireflective coating composition as mentioned above for the claims. The Patent Office has not provided any factual reasoning or scientific evidence to demonstrate otherwise.

The Patent Office has not explained why one skilled in the art, reading the disclosure of appellants' specification plus the scope of what would have been known to the skilled artisan, would not be able to make and use appellants' invention as presently claimed. It is well established that even a broad claim can be enabled by disclosure of a single embodiment. *Spectra-Physics*, 827 F.2d at 1533, 3 USPQ2d at 1743. Enablement requires that the specification teach those in the art to make and use the invention without 'undue experimentation'. *Wright*, 999 F.2d at 1561, 27 USPQ2d at 1513. That some experimentation may be required is not fatal; the issue is whether the amount of experimentation required is 'undue'.

On page 10, lines 19 to page 11, line 13, of their specification, appellants demonstrate the solubility evaluation of several bases in PGMEA (propylene glycol monomethyl ether acetate), a typical solvent for photoresist compositions.

On page 12, line 15 to page 14, line 5, of their specification, appellants provide an example between an antireflective coating composition containing a base that is considered insoluble in the solvent of a photoresist composition and an antireflective coating composition containing a base that is considered soluble in the solvent of a photoresist composition. At page 12, lines 24 to 30, appellants describe the antireflective coating compositions that were tested:

> The antireflective coatings were prepared using a co-polymer of benzyl methacrylate - mevalonic lactone methacrylate. The photoacid generator (PAG)

was triphenylsulfonium nonaflate, and the aforementioned base(s) and 4-hydroxy-4-methyl-2-pentanone as the solvent completed the antireflective coating formulations. The PAG content was kept at 1.7 wt. % of total solids of the antireflective coating formulations and the antireflective coating formulations were 1.65% total solids.

Table 2 on page 13 shows the results of example, which included coating the antireflective coating compositions onto wafers, baking the wafers, coating the antireflective coating with a photoresist, baking the coated wafer, exposing the coated wafer to radiation through a mask, post exposure baking the wafer, and then developing the wafer. As stated on page 14, lines 1 to 5, of appellants' specification:

> The data from Table 2 show that when the antireflective coating contains a base that is not soluble in the top layer resist solvent (whether that base is used alone or used together with a base that is soluble in the top layer resist solvent), the performance is better than those antireflective coatings which contain only a base that is soluble in the top layer resist solvent.

Thus, in order to make out a *prima facie* case under this section of the statute, the Patent Office must show that one of ordinary skill *in the antireflective coating composition used with photoresist composition arts* could not practice the claimed invention based on the information supplied in appellants' disclosure without undue experimentation, which requires more evidence than merely pointing out that specific "process conditions or parameters" have not been disclosed. This the Patent Office has not done.

The Patent Office has stated that the specification fails to show how to use a composition only containing one of the recited base compounds as encompassed by the

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claims is not supported. The Patent Office stated that the composition must provide an antireflection function as well as being coatable in the disclosed use in the specification.[6]

In view of the information provided by appellants in their specification, the Patent Office's basis for doubting the enablement of appellants' specification is not well founded.

The Patent Office fails to appreciate and understand that appellants' use of antireflective coating composition is clearly understood by the skilled artisan and that appellants have clearly defined and exemplified antireflective coating compositions in their specification. The Patent Office has not shown anything to the contrary.

Appellants have demonstrated how to use an antireflective coating composition, which a skilled artisan is deemed to know, using a recited base as encompassed by appellants' claims. Appellants' compositions provide an antireflection function and are coatable. See the discussion *supra* re the experiments shown in appellants' specification. The antireflective function is inherent to appellants' composition as those persons having ordinary skill in the art would understand and recognize the use of antireflective coating composition as used by appellants. The Patent Office has not provided any factual evidence or scientific reasoning to the contrary.

In the absence of a fact-based statement of a rejection based upon the relevant legal standards, the Patent Office has not sustained its burden of establishing a prima facie case of non-enablement. A disclosure which contains representative examples which provide reasonable assurance to one of ordinary skill in the art that the compositions falling within the scope of the claim can be made and possess utility is all that is required, absent any scientific reasons or evidence given by the Patent Office to doubt the accuracy

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[6] See final Office Action dated November 8, 2007, page 2, paragraph 1.

of appellants' statements in the specification. The Patent Office has not adequately considered and explained the state of the prior art, the nature of the invention, the working examples and the amount of guidance presented in the specification to support any conclusion that appellants' claims are not enabled. The Patent Office has not provided any scientific reasoning or factual evidence to support its conclusion of non-enablement.

The Patent Office has not sustained its burden of establishing a prima facie case of non-enablement. The statement of the rejection is plainly deficient. The rejection under 35 U.S.C. § 112, first paragraph, should be reversed.

Rejection of claims 1 to 9 and 32 to 37 under 35 U.S.C. § 102(b)

Hasegawa et al. (US6280898) or Sato et al. (US2002/0098440)

Anticipation under 35 U.S.C. § 102 requires the disclosure in a single prior art reference of each element of the claim under consideration. *In re Dillon*, 919 F.2d 688, 16 USPQ2d 1897, 1908 (Fed. Cir. 1990) (en banc), *cert. denied*, 500 U.S. 904 (1991). "A rejection for anticipation under section 102 requires that each and every limitation of the claimed invention be disclosed in a single prior art reference. *In re Spada,* 911 F.2d 705, 708, 15 USPQ2d 1655, 1657 (Fed. Cir. 1990). In addition, the reference must be enabling and describe the applicant's claimed invention sufficiently to have placed it in possession of a person of ordinary skill in the field of the invention. *Id.*" See *In re Paulsen*, 30 F.3d 1475, 1478-1479, 31 USPQ2d 1671, 1673 (Fed. Cir. 1994). "Under 35 U.S.C. § 102, every limitation of a claim must identically appear in a single prior art reference for it to anticipate the claim." *Gechter v. Davidson*, 116 F.3d 1454, 1457, 43 USPQ2d 1030, 1032 (Fed. Cir. 1997).

It is not enough, however, that the prior art reference discloses all the claimed elements in isolation. Rather, "[a]nticipation requires the presence in a single prior reference disclosure of each and every element of the claimed invention, *arranged as in the claim.*" *Lindemann Maschinenfabrik GmbH v. American Hoist & Derrick Co.*, 730 F.2d 1454, 1458, 221 USPQ 481, 485 (Fed. Cir. 1984) (emphasis added). "Every element of the claimed invention must be literally present, arranged as in the claim. The identical invention must be shown in as complete detail as is contained in the patent claim." *Richardson v. Suzuki Motor Co.*, 868 F.2d 1226, 1236, 9 USPQ2d 1913, 1920 (Fed. Cir. 1989) (citations omitted). See MPEP §2131. In other words, for anticipation under 35 U.S.C. § 102 to be found, each and every element set forth in the claim must be found, either expressly or inherently described, in a single prior art reference. *Id.*, citing to *Verdegaal Bros. v. Union Oil Co. of California*, 814 F.2d 628, 631, 2 USPQ2d 1051, 1053 (Fed. Cir. 1987), *cert. denied*, 484 U.S. 827 (1987) ("A claim is anticipated only if each and every element as set forth in the claim is found, either expressly or inherently described, in a single prior art reference."). The corollary is that "absence from the [prior art] reference of any claimed element negates anticipation." See *Kloster Speedsteel AB v. Crucible, Inc.*, 793 F.2d 1565, 1571, 230 USPQ 81, 84 (Fed. Cir. 1986), *cert. denied*, 479 U.S. 1034 (1987).

The Patent Office stated that Hasegawa et al. disclose coating compositions with polymers, photoacids, and basic amine compounds. The Patent Office stated that the layers would inherently reduce reflection if used as an underlayer to some extent.[7] There is no basis for the Patent Office's statement that the layers would inherently reduce reflection if used as an underlayer to some extent. In fact, there is no mention of antireflective coating or underlayer in Hasegawa et al. The Hasegawa et al. compositions are photoresist compositions, not antireflective coating compositions. Moreover,

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[7] As taken from the Office Action dated March 2, 2007, page 3, paragraph 7.

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Hasegawa et al. do not coat its photoresist compositions over antireflective coatings or underlayers; it coats on a silicon wafer (see column 35, lines 21 to 26; column 57, lines 44 to 46; and column 63, lines 28 to 29).

It is well known that inherency requires that the missing descriptive material be necessary present and that it would be so recognized by a person having ordinary skill in the art and cannot be established or based on conjecture and/or probabilities or possibilities. *Ex parte Skinner*, 2 USPQ2d 1788, 1789 (BPAI 1986). The mere fact that a certain thing *may* result from a given set of circumstances is not sufficient [to establish inherency]. *In re Rijckaert*, 9 F.3d 1531, 1534, 28 USPQ2d 1955, 1957 (Fed. Cir. 1993) (emphasis in original). "To establish inherency, the extrinsic evidence 'must make clear that the missing descriptive matter is necessarily present in the thing described in the reference, and that it would be so recognized by persons of ordinary skill. Inherency, however, may not be established by probabilities or possibilities. The mere fact that a certain thing may result from a given set of circumstances is not sufficient.' " *In re Robertson*, 169 F.3d 743, 745, 49 USPQ2d 1949, 1950-51 (Fed. Cir. 1999) (citations omitted). See MPEP § 2112, IV.

For a rejection under 35 U.S.C. § 102 rejection to be proper, the Patent Office must demonstrate that the applied prior art clearly and unequivocally discloses each and every element of a claimed invention, without any need for picking, choosing, and combining various disclosures therein. See *In re Arkley*, 455 F.2d 586, 587, 172 USPQ 524, 526 (CCPA 1972). "In relying upon the theory of inherency, the Patent Office must provide a basis in fact and/or technical reasoning to reasonably support the determination that the allegedly inherent characteristic *necessarily* flows from the teachings of the applied prior art." *Ex parte Levy*, 17 USPQ2d 1461, 1464 (BPAI 1990) (emphasis in original). Inherent anticipation requires that the claimed subject matter "necessarily and inevitably" occur.

See Schering Corp. v. Geneva Pharmaceuticals, 339 F.3d 1373, 1378, 67 USPQ2d 1664, 1668 (Fed. Cir. 2003).

The Patent Office's statement that the layers would inherently reduce reflection if used as an underlayer to some extent is without foundation. The Patent Office has failed to provide factual evidence or scientific reasoning to a person of ordinary skill in the art such that they would understand and recognize Hasegawa et al.'s photoresist compositions as being able to inherently reduce reflection if used as an underlayer. The Patent Office's statement that the layers would inherently reduce reflection if used as an underlayer to some extent is insufficient as this is just pure conjecture or a possibility and/or probability that something might result. This statement is not supported by any factual evidence or scientific reasoning and thus is not sufficient to justify or support a rejection of anticipation. There are no circumstances stated by the Patent Office that would cause a person having ordinary skill in the art to believe that Hasegawa et al.'s photoresist compositions would function like an underlayer having reflection. The Patent Office has not provided any support of any kind for its inherency theory. Inherency cannot be established based on conjecture and/or probabilities or possibilities. See *In re Oelrich*, 666 F.2d 578, 581, 212 USPQ 323, 326 (CCPA 1981). The Patent Office is resorting to speculation or unfounded assumptions to supply deficiencies in Hasegawa et al. This is not permissible.

Hasegawa et al. require that the components of its photoresist, including their basic compound, be soluble in the photoresist solvent ("The organic solvent used herein may be any organic solvent in which the base resin, photoacid generator, **and other components are soluble**."; column 21, lines 41 to 43; emphasis added), which is the opposite of appellants' invention. Appellants do not want the base in their antireflective coating compositions to be soluble in the solvent of the photoresist composition coated thereover. There is no teaching or suggestion in Hasegawa et al. to convert the photoresist

composition to an antireflective coating composition and then coat the antireflective coating composition with the photoresist composition with the base in the antireflective coating not being soluble in the solvent of the photoresist coating. Hasegawa et al. are the opposite, requiring that the components of its photoresist composition, including basis compounds, be soluble in the photoresist solvent that they use.

Where in Hasegawa et al. is the disclosure or teaching to a person having ordinary skill in the art to somehow convert Hasegawa et al.'s photoresist composition to an antireflective coating composition, then use the so-called antireflective coating composition with its photoresist composition, and not have the base soluble in the solvent of the photoresist composition thereof? Where is the inherent teaching to a person having ordinary skill in the art to do the same? There is none and the Patent Office has not made any demonstration thereof through factual evidence or scientific reasoning to support its conclusion. The Patent Office is resorting to impermissible speculation and/or unfounded assumptions to supply deficiencies in Hasegawa et al. The Patent Office has not pointed out where Hasegawa et al. specifically teach each and every element of appellants' invention as arranged in appellants' claims.

Thus, the Patent Office has not shown that Hasegawa et al. disclose an antireflective coating composition that is useful with a photoresist composition where the antireflective coating composition contains at least one base that is not soluble in a solvent of the photoresist composition with sufficient specificity to anticipate appellants' claims within the meaning of 35 U.S.C. § 102(b).

The same is true for Sato et al. Sato et al. state in paragraph [0111] that "**[t]he compositions of the present invention are dissolved in solvents dissolving the above-mentioned respective components**, and applied onto supports." (emphasis added), which is the opposite of what appellants' invention. Appellants do not want the

base in their antireflective coating compositions to be soluble in the solvent of the photoresist composition coated thereover. The Patent Office stated that Sato et al. disclose optional dyes, but they are for use in Sato et al.'s photoresist compositions. Sato et al. require the components of its photoresist composition to be soluble in the solvent that they use.

Where in Sato et al. is the disclosure or teaching to a person having ordinary skill in the art to somehow convert Sato et al.'s photoresist composition to an antireflective coating composition, then use the so-called antireflective coating composition with its photoresist composition, and not have the base soluble in the solvent of the photoresist composition thereof? Where is the inherent teaching to a person having ordinary skill in the art to do the same? There is none and the Patent Office has not made any demonstration thereof through factual evidence or scientific reasoning to support its conclusion. The Patent Office is resorting to impermissible speculation or unfounded assumptions to supply deficiencies in Sato et al. The Patent Office has not pointed out where Sato et al. specifically teach each and every element of appellants' invention as arranged in appellants' claims.

Thus, the Patent Office has not shown that Sato et al. disclose an antireflective coating composition that is useful with a photoresist composition where the antireflective coating composition contains at least one base that is not soluble in a solvent of the photoresist composition with sufficient specificity to anticipate appellants' claims within the meaning of 35 U.S.C. § 102(b).

Like Hasegawa et al., Sato et al. do not mention antireflective coatings or underlayers. Sato et al. also coat directly onto wafers ("The above-mentioned compositions are applied onto substrates (for example, silicon/silicon dioxide coating) ...

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. [0118]; "The resulting positive photoresist composition solution was applied onto a silicon wafer with a spin coater ... . [0134]).

The Patent Office stated that Sato et al. disclose coating compositions comprising polymers, photoacids, optional dyes and basic amine compounds including purine[8], but does not describe how this is now appellants' claimed invention or how a person having ordinary skill in the art would arrive at appellants' invention. The coating compositions of Sato et al. are photoresist compositions and Sato et al. do not demonstrate antireflective coating properties. Moreover, the aforementioned components of Sato et al. have to be soluble in the photoresist solvent of Sato et al. See paragraph [0111] of Sato et al. The Patent Office has not made any demonstration of this nor has it provided any factual evidence or scientific reasoning thereto.

The Patent Office has not met the burden of making out a prima facie case of anticipation by pointing out where Hasegawa et al. or Sato et al. clearly and unequivocally describe each and every element of appellants' claimed invention in the order as presented by appellants in their claims.

Appellants' claims 1 to 9 and 32 to 37 require an antireflective coating composition that contains a base that is not soluble in the solvent of the photoresist with which the antireflective coating composition is used. Thus, Hasegawa et al. or Sato et al. must meet this limitation in order to establish a prima facie case of anticipation. In order to show that the compositions of Hasegawa et al. or Sato et al. inherently meet the limitation, the Patent Office must establish by factual evidence or scientific reasoning that such limitation is necessarily present in the composition of Hasegawa et al. or Sato et al. and that it would be recognized as such by one of ordinary skill in the

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[8] From Office Action dated March 2, 2007, page 3, paragraph 7.

art. The mere fact that a certain thing might result from a given set of circumstances is not sufficient. The Patent Office's statement that the layers would inherently reduce reflection if used as an underlayer to some extent is insufficient as this is just pure conjecture or a possibility and/or probability that something might result. The Patent Office's statement is not supported by any factual evidence or scientific reasoning and thus is not sufficient to justify or support a rejection of anticipation.

The Patent Office stated in the Office Action that the intended use of the compositions in the present application do not materially distinguish them from the compositions of Hasegawa et al. or Sato et al. The Patent Office further stated that the compositions of Hasegawa et al. or Sato et al. being materially the same as those encompassed by the claims, would have the same properties.[9]

However, the Patent Office has not articulated nor provided any rationale as to how the compositions of Hasegawa et al. or Sato et al. would function as an antireflective coating composition having a base that is not soluble in the solvent of a photoresist composition with which it is used. The Patent Office has not demonstrated that Hasegawa et al. or Sato et al. teach an antireflective coating composition that has a base that is not soluble in the solvent of a photoresist composition with which it is used. The Patent Office has not established with sufficient specificity how either Hasegawa et al. or Sato et al. substantially corresponds to each claim feature to support any inference that Hasegawa et al. or Sato et al. meet the claim features of appellants' invention in the order presented therein. The Patent Office has not cited passages within either Hasegawa et al. or Sato et al. that would cause a person having ordinary skill in the art to reach the conclusion that the Patent Office has reached.

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[9] See the Office Action of August 1, 2007, paragraph 4.

Hasegawa et al. and Sato et al. each require that the components in their photoresist compositions be soluble in the photoresist solvent used in their respective photoresist compositions. This clearly teaches away from appellants' claims. Neither Hasegawa et al. nor Sato et al. teach, disclose, or suggest to the skilled artisan how to convert their photoresist compositions to antireflective coating compositions and provide the antireflective coating composition with a base, where the base is not soluble in the solvent of the photoresist composition.

The Patent Office has not met its burden of making out a prima facie case of anticipation by pointing out where each and every element of appellants' claimed invention, arranged as required by the claims, is described identically in either Hasegawa et al. or Sato et al., either expressly or under the principles of inherency. It appears the Patent Office is relying on suggestions of the references to assert the requirements of the present invention are inherently possessed by Hasegawa et al. or Sato et al. Yet, the supposed suggestions in Hasegawa et al. or Sato et al. have not been identified by the Patent Office. Inherency cannot be based upon conjecture or probabilities and/or possibilities. Suggestions and inferences which could have been derived from a reference are not proper basis for formulating an anticipation rejection under § 102.

Contrary to the Patent Office's statement that appellants' claims only materially require the presence of basic compounds, appellants' claims require that the basic compounds be in an antireflective coating composition that is useful with a photoresist composition and that the base used in the antireflective coating composition is not soluble in a solvent of the photoresist composition. This has been clearly demonstrated above.

The Patent Office's view that the compositions of Hasegawa et al. or Sato et al. as being materially the same as those of appellants' claims or the bases disclosed therein would be insoluble in some solvents falls short in establishing a prima facie case of anticipation based on inherency since such view is based on conjecture or probability and/or possibility. The Patent Office has not provided any support, by way of identifying text in either Hasegawa et al. or Sato et al., that the compositions of either are materially the same as appellants. Thus, the Patent Office has not established that Hasegawa et al. or Sato et al. anticipate an antireflective coating composition that has a base that is not soluble in the solvent of a photoresist composition with which it is used as claimed by appellants.

The Patent Office also stated that the bases (of Hasegawa et al. and Sato et al.?) would be insoluble in some solvents.[10] However, the Patent Office provided no factual evidence or scientific reasoning for such a statement. As stated above, both Hasegawa et al. and Sato et al. contradict the Patent Office in that they both require that the components of their system be _soluble_ in the solvents therein. The Patent Office has not proven or demonstrated otherwise.

The Patent Office also stated that the claims do not specify particular solvents.[11] Appellants have specified that the base in the antireflective coating is not soluble in the solvent of the photoresist composition. The Patent Office has not provided a basis for requiring appellants to particularly identify the solvents as a functional description of the solvent (a photoresist solvent) and its relation to the base (the base is not soluble in the photoresist solvent), the correlation of solubility being shown in appellants' specification (see page 4, lines 10 -19; page 5, lines 11 - 15; page 6, lines 14 - 31; page 7, lines 4 -

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[10] See the Office Action dated August 1, 2007.
[11] _Id._

15; page 8, lines 14 - 31; and page 9, line 1 to page 11, line 13). Appellants specify that the base is not soluble in the solvent of the photoresist composition. Nothing more need be stated.

The dispositive question is whether <u>one skilled in the art</u> would reasonably understand or infer from the teachings of either Hasegawa et al. or Sato et al. that every claim element is disclosed therein. Hasegawa et al. teach that components in its system are soluble in the organic solvent used therein. Hasegawa et al. make no mention of antireflective coatings and its use with photoresist compositions. Hasegawa et al. make no mention that the base in antireflective coatings is not soluble in the solvent of the photoresist compositions. Sato et al. teach that the compositions therein are dissolved in solvents which dissolve the components therein. Sato et al. make no mention of antireflective coatings and its use with photoresist compositions. Sato et al. make no mention that the base in antireflective coatings is not soluble in the solvent of the photoresist compositions. Neither Hasegawa et al. nor Sato et al. teach, in a manner reasonably understandable or inferable by one skilled in the art, an antireflective coating composition used with a photoresist composition where the antireflective coating composition has at least one base which is not soluble in a solvent of the photoresist composition. The Patent Office provides no factual evidence or scientific reasoning or citations in Hasegawa et al. or Sato et al. to state otherwise.

The fatal flaw in the Patent Office's anticipation rejection of appellants' claims over Hasegawa et al. or Sato et al. is the Patent Office's failure to establish either Hasegawa et al. or Sato et al. as providing an antireflective coating composition that is useful with a photoresist composition where the antireflective coating composition contains a least one base that is not soluble in a solvent of the photoresist composition. Neither Hasegawa et al. nor Sato et al. provide a disclosure with sufficient specificity to constitute a description of appellants' claimed invention within the purview of 35 U.S.C. § 102.

Anticipation means being able to literally read each and every word of a claim upon a sufficiently concrete embodiment that is identically disclosed or described in the prior art. Appellants should be able to expect that at a minimum, the Patent Office would explain with some degree of specificity where, in either Hasegawa et al. or Sato et al., it finds an "identically disclosed or described" concrete embodiment upon which appellants' claim read. In the present case, this the Patent Office has not done.

Neither Hasegawa et al. nor Sato et al. disclose or teach an antireflective coating composition that contains a base which is not soluble in the solvent of a photoresist used with the antireflective coating composition. The absence of these elements negates any anticipation rejection.

The rejection of claims 1 to 9 and 32 to 37 over either Hasegawa et al. or Sato et al. should be reversed.

Rejection of claims 1 to 9 and 32 to 37 under 35 U.S.C. § 102(e)

Nishimura et al. (US6800414)

Anticipation under 35 U.S.C. § 102 requires the disclosure in a single prior art reference of each element of the claim under consideration. *In re Dillon*, 919 F.2d 688, 16 USPQ2d 1897, 1908 (Fed. Cir. 1990) (en banc), *cert. denied*, 500 U.S. 904 (1991). "A rejection for anticipation under section 102 requires that each and every limitation of the claimed invention be disclosed in a single prior art reference. *In re Spada*, 911 F.2d 705, 708, 15 USPQ2d 1655, 1657 (Fed. Cir. 1990). In addition, the reference must be enabling and describe the applicant's claimed invention sufficiently to have placed it in possession of a person of ordinary skill in the field of the invention. *Id.*" See *In re*

Paulsen, 30 F.3d 1475, 1478-1479, 31 USPQ2d 1671, 1673 (Fed. Cir. 1994). "Under 35 U.S.C. § 102, every limitation of a claim must identically appear in a single prior art reference for it to anticipate the claim." *Gechter v. Davidson*, 116 F.3d 1454, 1457, 43 USPQ2d 1030, 1032 (Fed. Cir. 1997).

It is not enough, however, that the prior art reference discloses all the claimed elements in isolation. Rather, "[a]nticipation requires the presence in a single prior reference disclosure of each and every element of the claimed invention, *arranged as in the claim. Lindemann Maschinenfabrik GmbH v. American Hoist & Derrick Co.*, 730 F.2d 1454, 1458, 221 USPQ 481, 485 (Fed. Cir. 1984) (emphasis added). "Every element of the claimed invention must be literally present, arranged as in the claim. The identical invention must be shown in as complete detail as is contained in the patent claim." *Richardson v. Suzuki Motor Co.*, 868 F.2d 1226, 1236, 9 USPQ2d 1913, 1920 (Fed. Cir. 1989) (citations omitted). See MPEP §2131. In other words, for anticipation under 35 U.S.C. § 102 to be found, each and every element set forth in the claim must be found, either expressly or inherently described, in a single prior art reference. *Id.*, citing to *Verdegaal Bros. v. Union Oil Co. of California*, 814 F.2d 628, 631, 2 USPQ2d 1051, 1053 (Fed. Cir. 1987), *cert. denied*, 484 U.S. 827 (1987). ("A claim is anticipated only if each and every element as set forth in the claim is found, either expressly or inherently described, in a single prior art reference."). The corollary is that "absence from the [prior art] reference of any claimed element negates anticipation." See *Kloster Speedsteel AB v. Crucible, Inc.*, 793 F.2d 1565, 1571, 230 USPQ 81, 84 (Fed. Cir. 1986), *cert. denied*, 479 U.S. 1034 (1987).

Like Hasegawa et al. and Sato et al. as discussed above and incorporating the remarks therein, Nishimura et al. require that the components in its photoresist composition be soluble in its solvent ("[t]he radiation-sensitive resin composition of the present invention is prepared as a **composition solution by dissolving the**

composition in a solvent … ."(see column 51, lines 31 to 33) (emphasis added)), which is the opposite of appellants' invention. Appellants do not want the base in their antireflective coating compositions to be soluble in the solvent of the photoresist composition coated thereover. Nowhere do Nishimura et al. state that bases that it uses in the photoresist composition, which are to be dissolved in its composition solvent (see above), are not soluble in the solvent of the photoresist composition.

The Patent Office stated that Nishimura et al. disclose halation inhibitors[12], but they are for use in Nishimura et al.'s photoresist compositions. In fact, Nishimura et al. provide that their photoresist compositions can be used with an additional antireflection film ("In order to bring out latent capability of the radiation-sensitive resin composition of the present invention, an organic or inorganic anti-reflection film may be formed on a substrate as disclosed in Japanese Patent Publication No. 12452/1994, for example."; see column 52, lines 61 to 65). There is nothing in Nishimura et al. that disclose that the anti-reflection film contains a base and that if there was a base that it would not be soluble in the solvent of the photoresist composition. The Patent Office is resorting to speculation or unfounded assumptions to supply deficiencies in Nishimura et al. This is not permissible.

The Patent Office stated that Nishimura et al. disclose coating compositions with polymers, photoacids, optional dyes and basic amine compounds including purines and benzimidazoles[13], but does not describe how this is now appellants' claimed invention or how a person having ordinary skill in the art would arrive at appellants' invention. "[F]or the instant rejection under 35 U.S.C. § 102(e) to have been proper, [Nishimura et al.] must clearly and unequivocally disclose the claimed [composition] or direct those skilled in the art to the [composition] without *any* need for picking, choosing, and combining various

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[12] *Id.*
[13] From Office Action dated March 2, 2007, page 3, paragraph 7.

disclosures not directly related to each other by the teachings of [Nishimura et al.]" *Arkley*, 455 F.2d at 587, 172 USPQ at 526.

The Patent Office has not met its burden of making out a prima facie case of anticipation by pointing out where Nishimura et al. clearly and unequivocally describe each and every element of appellants' claimed invention, in the order as presented by appellants in their claims, either expressly or under the principles of inherency. It appears the Patent Office is relying on suggestions of the references to assert the requirements of the present invention are inherently possessed by Nishimura et al. Yet, the supposed suggestions in Nishimura et al. have not been identified by the Patent Office. Inherency cannot be based upon conjecture or probabilities and/or possibilities. Suggestions and inferences which could have been derived from a reference are not proper basis for formulating an anticipation rejection under § 102.

The Patent Office has to explain where a skilled artisan would read or find such a teaching or suggestion. The Patent Office has not provided any evidence that the bases would have the same solubility properties and is only basing such a conclusion on probabilities or conjecture. Nor has the Patent Office shown that Nishimura et al. disclose an antireflective coating composition which contains a base that is not soluble in the solvent of a photoresist composition used with the antireflective coating compositions. The Patent Office is resorting to impermissible speculation or unfounded assumptions to supply deficiencies in Nishimura et al.

For a document to anticipate a claim, every element of the claimed invention must be literally present, arranged as in the claim. Nishimura et al. do not disclose every element of appellants' claims. For the Patent Office to support its anticipation rejection, the Patent Office has to demonstrate, citing column and line, where in Nishimura et al. is it stated that the base in the antireflective coating composition is not

soluble in the solvent of the photoresist composition. The Patent Office has not done so and cannot do so since Nishimura et al. do not make such a statement or assertion. The anticipation analysis asks solely whether the prior art document discloses and enables the claimed invention. Nishimura et al. fail in both respects.

The Patent Office also stated that the bases (of Nishimura et al.?) would be insoluble in some solvents.[14] However, the Patent Office provided no factual evidence or scientific reasoning for such a statement. As stated above, Nishimura et al. contradict the Patent Office in that it requires that the components of their system be soluble in the solvents therein. The Patent Office has not proven or demonstrated otherwise.

The dispositive question is whether one skilled in the art would reasonably understand or infer from the teachings of Nishimura et al. that every claim element is disclosed therein. Nishimura et al. teach that components in its system are soluble in the organic solvent used therein. Nishimura et al. mention using an antireflective coating with its photoresist compositions, but makes no mention or discussion of the components in the antireflective coating. While Nishimura et al. do mention the use of halation inhibitors, it is for inclusion in its photoresist composition, not as a separate antireflective coating composition which is then overcoated by its photoresist composition. Nishimura et al. fail to teach, in a manner reasonably understandable or inferable by one skilled in the art, an antireflective coating composition used with a photoresist composition where the antireflective coating composition has at least one base which is not soluble in a solvent of the photoresist composition. The Patent Office provides no factual evidence or scientific reasoning or citations in Nishimura et al. to state otherwise.

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[14] *Id.*

The fatal flaw in the Patent Office's anticipation rejection of appellants' claims over Nishimura et al. is the Patent Office's failure to establish Nishimura et al. as providing an antireflective coating composition that is useful with a photoresist composition where the antireflective coating composition contains a least one base that is not soluble in a solvent of the photoresist composition. Nishimura et al. do not provide a disclosure with sufficient specificity to constitute a description of appellants' claimed invention within the purview of 35 U.S.C. § 102.

Anticipation means being able to literally read each and every word of a claim upon a sufficiently concrete embodiment that is identically disclosed or described in the prior art. Appellants should be able to expect that at a minimum, the Patent Office would explain with some degree of specificity where, in Nishimura et al., it finds an "identically disclosed or described" concrete embodiment upon which appellants' claim read. In the present case, this the Patent Office has not done.

Nishimura et al. do not disclose or teach an antireflective coating composition that contains a base which is not soluble in the solvent of a photoresist used with the antireflective coating composition. The absence of these elements negates any anticipation rejection.

The rejection of claims 1 to 9 and 32 to 37 over Nishimura et al. should be reversed.

CONCLUSION

Appellants submit that all pending claims 1 to 9 and 32 to 37 are patentable and that the present application is in condition for allowance.

Serial No. 10/677,318
Filed: October 3, 2003
Appellant's Brief under 37 C.F.R. § 41.67

The Commissioner for Patents is authorized to charge the requisite fee for appellants' Appeal Brief of $510.00 (37 C.F.R. § 41.20 (b)(2)) to Deposit Account No. 50-3309. Any underpayment may be charged or overpayment may be credited to Deposit Account No. 50-3309.

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APPENDIX 1 - APPEALED CLAIMS

1.   (previously presented)   An antireflective coating composition useful with a photoresist composition comprising an antireflective coating composition having at least one base which is not soluble in a solvent of the photoresist composition, wherein said at least one base which is not soluble in a solvent of the photoresist composition is selected from optionally substituted aminophylline, optionally substituted purine, optionally substituted 2,6-diaminopurine, optionally substituted 6-(dimethylamino)purine, optionally substituted xanthine, optionally substituted guanine, optionally substituted hypoxanthine, optionally substituted adenine, optionally substituted caffeine, optionally substituted theophylline, optionally substituted theobromine, optionally substituted cytosine, optionally substituted cytisine, optionally substituted thymine, optionally substituted azapyridines, optionally substituted 8-azaguanines, optionally substituted 2-hydroaminoazines, and mixtures thereof.

2.   (original) The antireflective coating composition of claim 1 wherein the base has a solubility of less than or equal to 0.2 wt. % in a solvent of the photoresist composition.

3.   (original) The antireflective coating composition of claim 1 wherein the base has a solubility of less than or equal to 0.15 wt. % in a solvent of the photoresist composition.

4.   (original) The antireflective coating composition of claim 1 wherein the base has a solubility of less than or equal to 0.1 wt. % in a solvent of the photoresist composition.

5.   (original) The antireflective coating composition of claim 1 wherein only one base which is not soluble in a solvent of the photoresist composition is present.

6.   (original) The antireflective coating composition of claim 1 wherein the base is present in an amount of from about 0.001 to about 15 wt % based on the solids of the antireflective coating composition.

7.   (original) The antireflective coating composition of claim 6 wherein the base is present in an amount of from about 0.001 to about 10 wt % based on the solids of the antireflective coating composition.

8.   (original) The antireflective coating composition of claim 1 which further comprises at least one base which is soluble in a solvent of the photoresist composition.

9.   (original) The antireflective coating composition of claim 1 which further comprises one or more components selected from polymers, crosslinking materials, solvents, photoacid generators, dyes and surface active agents.

Claims 10 to 31   (canceled)

32.   (original) A method for forming an antireflective coating layer comprising the step of coating a substrate with the antireflective coating composition of claim 1.

33.   (original) The method of claim 32 wherein for the antireflective coating composition, the base has a solubility of less than or equal to 0.2 wt. % in a solvent of the photoresist composition.

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34.   (original) The method of claim 32 wherein for the antireflective coating composition, the base has a solubility of less than or equal to 0.15 wt. % in a solvent of the photoresist composition.

35.   (original) The method of claim 32 wherein for the antireflective coating composition, the base has a solubility of less than or equal to 0.1 wt. % in a solvent of the photoresist composition.

36.   (original) The method of claim 32 wherein for (a) the base is present in an amount of from about 0.001 to about 15 wt % based on the solids of the antireflective coating composition.

37.   (original) The method of claim 36 wherein the base is present in an amount of from about 0.001 to about 10 wt % based on the solids of the antireflective coating composition.

Claims 38 to 46   (canceled)

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APPENDIX 2 - EVIDENCE RELIED UPON

None

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APPENDIX 3 - RELATED PROCEEDINGS

None

APPENDIX 4

US005886102A

United States Patent [19]

Sinta et al.

[11] **Patent Number:** **5,886,102**

[45] **Date of Patent:** **Mar. 23, 1999**

[54] **ANTIREFLECTIVE COATING COMPOSITIONS**

[75] Inventors: **Roger F. Sinta**, Woburn; **Timothy G. Adams**, Sudbury; **James Michael Mori**, Dorchester, all of Mass.

[73] Assignee: **Shipley Company, L.L.C.,** Marlborough, Mass.

[21] Appl. No.: **665,019**

[22] Filed: **Jun. 11, 1996**

[51] **Int. Cl.⁶** **G03F 7/11**; C08L 33/08; C08L 33/10; C08L 33/04

[52] **U.S. Cl.** **525/154**; 525/154; 525/330.3; 525/330.4; 525/330.5; 525/330.6; 430/271.1

[58] **Field of Search** 525/154, 106, 525/130, 185, 194, 330.3, 330.4, 330.5, 330.6; 430/271.1

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[57] **ABSTRACT**

The invention provides new light absorbing crosslinking compositions suitable for use as an antireflective composition (ARC), particularly for deep UV applications. The ARCs of the invention in general comprise a crosslinker and novel ARC resin binders that effectively absorb reflected deep UV exposure radiation.

9 Claims, No Drawings

ANTIREFLECTIVE COATING COMPOSITIONS

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to compositions that reduce reflection of exposing radiation from a substrate back into an overcoated photoresist layer. More particularly, the invention relates to antireflective coating compositions that contain a resin binder components that effectively absorbs deep UV exposure radiation.

2. Background Art

Photoresists are photosensitive films used for transfer of an image to a substrate. A coating layer of a photoresist is formed on a substrate and the photoresist layer is then exposed through a photomask to a source of activating radiation. The photomask has areas that are opaque to activating radiation and other areas that are transparent to activating radiation. Exposure to activating radiation provides a photoinduced chemical transformation of the photoresist coating to thereby transfer the pattern of the photomask to the photoresist coated substrate. Following exposure, the photoresist is developed to provide a relief image that permits selective processing of a substrate.

A photoresist can be either positive-acting or negative-acting. For most negative-acting photoresists, those coating layer portions that are exposed to activating radiation polymerize or crosslink in a reaction between a photoactive compound and polymerizable reagents of the photoresist composition. Consequently, the exposed coating portions are rendered less soluble in a developer solution than unexposed portions. For a positive-acting photoresist, exposed portions are rendered more soluble in a developer solution while areas not exposed remain comparatively less developer soluble. Photoresist compositions are known to the art and described by Deforest, *Photoresist Materials and Processes*, McGraw Hill Book Company, New York, ch. 2, 1975 and by Moreay, *Semiconductor Lithography, Principles, Practices and Materials*, Plenum Press, New York, ch. 2 and 4, both incorporated herein by reference for their teaching of photoresist compositions and methods of making and using the same.

A major use of photoresists is in semiconductor manufacture where an object is to convert a highly polished semiconductor slice, such as silicon or gallium arsenide, into a complex matrix of electron conducting paths, preferably of micron or submicron geometry, that perform circuit functions. Proper photoresist processing is a key to attaining this object. While there is a strong interdependency among the various photoresist processing steps, exposure is believed to be one of the more important steps in attaining high resolution photoresist images.

Reflection of activating radiation used to expose a photoresist often poses limits on resolution of the image patterned in the photoresist layer. Reflection of radiation from the substrate/photoresist interface can produce variations in the radiation intensity in the photoresist during exposure, resulting in non-uniform photoresist linewidth upon development. Radiation also can scatter from the substrate/photoresist interface into regions of the photoresist where exposure is not intended, again resulting in linewidth variations. The amount of scattering and reflection will typically vary from region to region, resulting in further linewidth non-uniformity.

Reflection of activating radiation also contributes to what is known in the art as the "standing wave effect". To

eliminate the effects of chromatic aberration in exposure equipment lenses, monochromatic or quasi-monochromatic radiation is commonly used in photoresist projection techniques. Due to radiation reflection at the photoresist/substrate interface, however, constructive and destructive interference is particularly significant when monochromatic or quasi-monochromatic radiation is used for photoresist exposure. In such cases the reflected light interferes with the incident light to form standing waves within the photoresist. In the case of highly reflective substrate regions, the problem is exacerbated since large amplitude standing waves create thin layers of underexposed photoresist at the wave minima. The underexposed layers can prevent complete photoresist development causing edge acuity problems in the photoresist profile. The time required to expose the photoresist is generally an increasing function of photoresist thickness because of the increased total amount of radiation required to expose an increased amount of photoresist. However, because of the standing wave effect, the time of exposure also includes a harmonic component which varies between successive maximum and minimum values with the photoresist thickness. If the photoresist thickness is non-uniform, the problem becomes more severe, resulting in variable linewidths.

Variations in substrate topography also give rise to resolution-limiting reflection problems. Any image on a substrate can cause impinging radiation to scatter or reflect in various uncontrolled directions, affecting the uniformity of photoresist development. As substrate topography becomes more complex with efforts to design more complex circuits, the effects of reflected radiation become more critical. For example, metal interconnects used on many microelectronic substrates are particularly problematic due to their topography and regions of high reflectivity.

With recent trends towards high-density semiconductor devices, there is a movement in the industry to shorten the wavelength of exposure sources to deep ultraviolet (DUV) light (300 nm or less in wavelength), KrF excimer laser light (248.4 nm), ArF excimer laser light (193 nm), electron beams and soft x-rays. The use of shortened wavelengths of light for imaging a photoresist coating has generally resulted in increased reflection from the upper resist surface as well as the surface of the underlying substrate. Thus, the use of the shorter wavelengths has exacerbated the problems of reflection from a substrate surface.

Another approach used to reduce the problem of reflected radiation has been the use of a radiation absorbing layer interposed between the substrate surface and the photoresist coating layer. See, for example, PCT Application WO 90/03598, EPO Application No. 0 639 941 A1 and U.S. Pat. Nos. 4,910,122, 4,370,405 and 4,362,809, all incorporated herein by reference for their teaching of antireflective (antihalation) compositions and the use of the same. Such layers have also been referred to in the literature as antireflective layers or ARCs (antireflective compositions).

The ARC of the above cited European Application 639 941 A1 comprises a compound having one or more glycidyl groups in the molecule, at least one anthracene derivative derivatized so as to cross-link with the compound having one or more glycidyl groups and a solvent. In use, an antireflective coating is coated onto a substrate and cured whereby the derivatized anthracene acts as a cross-linking agent with the compound having the glycidyl substitution. That disclosed ARC can exhibit certain disadvantages, particularly with respect to stability or consistency. Specifically, compounds having glycidyl substitution are relatively reactive, e.g., the glycidyl groups may react with each other

or with the derivatized anthracene. This can result in a change in viscosity of the ARC coating solution during storage which will alter coating characteristics. In use, the described ARCs are coated onto a substrate and then cured to induce crosslinking between the derivatized anthracene and the glycidyl groups of the glycidyl containing compound. Cure conditions include heating to a temperature of from 150° to 230° C. for up to 30 minutes. At these temperatures, the derivatized anthracene may evaporate or sublime from the coating together with the solvents for the coating composition. Since the anthracene derivative is both a chromophore and a crosslinking agent, a reduction in its concentration in the ARC can lead to unpredictable absorption characteristics and unpredictable dissolution properties.

In Shipley Company's European Application 542 008 A1 highly useful antihalation (antireflective) compositions are disclosed that comprise a resin binder and a crosslinker compound.

While it has been found that prior ARC compositions may be effective for many antireflective applications, prior compositions also may pose some potential performance limitations, e.g. when the antireflective compositions are used with resist compositions to pattern features of submicron or sub-half micron dimensions. In particular, use of at least some prior antireflective compositions has resulted in undercutting of a developed resist relief image, known in the art as "notching". Another problem has been "footing", i.e. the failure to clear during development that results in an upwardly tapering relief image sidewall. Both notching and footing can compromise the resolution of the image patterned onto the underlying substrate.

It thus would be desirable to have new antireflective coating compositions.

SUMMARY OF THE INVENTION

The present invention provides new light absorbing crosslinking compositions suitable for use as an ARC, particularly for deep UV applications. The ARCs of the invention in general comprise a crosslinker and a resin binder that effectively absorbs deep Uw exposure radiation to reduce reflections of same.

Resin binders of ARCs of the invention contain one or more moieties that are chromophores for the exposure radiation of an overcoated resist composition, i.e. the moieties are capable of absorbing exposure radiation to thereby reduce reflections. For example, for preferred antireflective compositions used with a deep UV (DUV) photoresist, preferred chromophores include anthracenyl, particularly alkylene anthracene esters such as pendant groups of the formula —(C=O)O(CH$_2$)$_n$ anthracene, wherein n is an integer from 1 to about 6. Other preferred chromophores include quinolinyl and ring-substituted quinolinyl derivatives such as hydroxyquinolinyl, phenanthrenyl and acridine groups. Suitably about 5 to 90 percent of the units of a resin comprise such a chromophore, more preferably about 10 to 80 percent. Preferred resin binders of the invention have an optical density of at least about 4 units/μ at 248 nm. Preferred resin binders also are capable of reaction with the crosslinker component, e.g. by a hydroxy or carboxy moiety on the resin or a "masked" moiety such as an ester that can generate such a reactive group in the presence of acid or otherwise.

The antireflective composition resin binder with chromophore moieties suitably is a copolymer and is prepared by polymerizing two or more different monomers where at least one of the monomers includes a chromophore group. It has

been found that this synthesis provides distinct advantages over finctionalization of a preformed polymer to add chromophore groups. For example, the synthesis of the invention avoids further reaction steps of grafting the chromophore units onto a preformed polymer as well as one or more subsequent purification steps. The synthesis also permits precise tailoring of the composition of the formed resin.
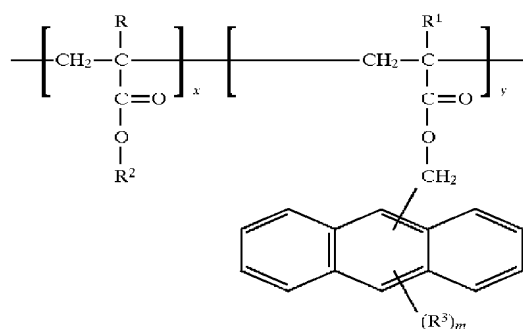
Also, the synthesis of the invention enables good control of the quantity of chromophore units on a polymer. In contrast, grafting of chromophore units onto a preformed resin often provides a resin mixture of polymers with varying percentages of chromophore. Such differing quantities of chromophores unit can compromise resolution of an image patterned into an overcoated photoresist layer as the chromophore differences may result in essentially random reflections of exposure radiation. The synthesis of the invention also enables preparation of a greater variety of types of polymers. Grafting chromophore units onto at least some types of preformed polymers may be quite difficult, or simply not possible, particularly in larger scale productions. For example, it can be particularly difficult to drive the reaction to completion resulting in undesired products which must be removed from desired materials.

The invention further provides methods for forming a relief image and novel articles of manufacture comprising substrates coated with an ARC composition of the invention alone or in combination with a photoresist composition. Other aspects of the invention are disclosed infra.

DETAILED DESCRIPTION OF THE INVENTION

The resin binder component of the antireflective compositions of the invention are preferably used with deep UV imaging systems and will effectively absorb reflections in the deep UV range (typically from about 100 to 300 nm). Thus, the resin binder preferably contains units that are deep UV chromophores, i.e. units that absorb deep UV radiation. Highly conjugated moieties are generally suitable chromophores. Aromatic groups, particularly polycyclic hydrocarbon or heterocyclic units, are typically preferred deep UV chromophores, e.g. groups having from two to three or four fussed or separate rings with 3 to 8 ring members in each ring and zero to three N, O or S atoms per ring. Such chromophores include substituted and unsubstituted phenanthryl, substituted and unsubstituted anthracyl, substituted and unsubstituted acridine, substituted and unsubstituted naphthyl, substituted and unsubstituted quinolinyl and ring-substituted quinolinyls such as hydroxyquinolinyl groups. Substituted or unsubstituted anthracyl groups are particularly preferred. For example, preferred resin binders have pendant anthracyl groups, particularly acrylic resins of the following Formula (I):

$$-\left[CH_2-\underset{\underset{\underset{R^2}{|}}{\underset{|}{O}}}{\overset{\overset{R}{|}}{\underset{|}{C}}}\right]_x\left[CH_2-\underset{\underset{\underset{CH_2}{|}}{\underset{|}{O}}}{\overset{\overset{R^1}{|}}{\underset{|}{C}}}\right]_y \quad (I)$$

(R³)ₘ

wherein each R and R^1 is independently a hydrogen or a substituted or unsubstituted alkyl group having from 1 to about 8 carbon atoms, preferably substituted or unsubstituted C_{1-6} alkyl;

each R^2 is independently substituted or unsubstituted alkyl having 1 to about 10 carbon atoms, more typically 1 to about 6 carbons;

each R^3 may be independently halogen (particularly F, Cl and Br), alkyl having 1 to about 8 carbon atoms, alkoxy having 1 to about 8 carbon atoms, alkenyl having 2 to about 8 carbon atoms, alkynyl having 2 to about 8 carbon atoms, cyano, nitro, etc.;

m is an integer of from 0 (where the anthracyl ring is fully hydrogen-substituted) to 9, and preferably m is 0, 1 or 2;

x is the mole fraction or percent of alkyl acrylate units in the polymer and preferably is from about 10 to about 80 percent; and y is the mole fraction or percent of anthracene units in the polymer and preferably is from about 5 to 10 to 90 percent. The polymer also may contain other units if desired, but preferably the polymer will contain at least about 10 mole percent of anthracene units. Hydroxyalkyl is a particularly preferred R^2 group, especially alkyl having a primary hydroxy group such as where R^2 is 2-hydroxyethylene (—CH_2CH_2OH). Preferably the resin binder contains 9-(methylene)anthracene ester units.

Another preferred resin binder comprises substituted or unsubstituted quinolinyl or a quinolinyl derivative that has one or more N, O or S ring atoms such as a hydroxyquinolinyl. The polymer may contain other units such as carboxy and/or alkyl ester units pendant from the polymer backbone. A particularly preferred ARC resin binder is an acrylic polymer of the following Formula (II):

$$-\left[CH_2-\underset{\underset{\underset{R^6}{|}}{\underset{|}{O}}}{\overset{\overset{R^4}{|}}{\underset{|}{C}}}\right]_{x'}\left[CH_2-\underset{\underset{\underset{W}{|}}{\underset{|}{O}}}{\overset{\overset{R^5}{|}}{\underset{|}{C}}}\right]_{y'} \quad (II)$$

(R⁷)ₙ

wherein each R^4 and R^5 is independently a hydrogen or a substituted or unsubstituted alkyl group having from 1 to about 8 carbon atoms, preferably substituted or unsubstituted C_{1-6} alkyl;
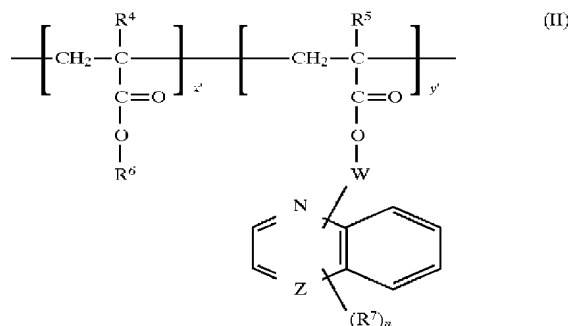
each R^6 is independently substituted or unsubstituted alkyl having 1 to about 10 carbon atoms, more typically 1 to about 6 carbons;

W is a bond or substituted or unsubstituted alkylene having 1 to about 4 carbons, and preferably is a bond;

Z is a carbon, nitrogen, oxygen or sulfur;

each R^7 may be independently halogen (particularly F, Cl and Br), alkyl having 1 to about 8 carbon atoms, alkoxy having 1 to about 8 carbon atoms, alkenyl having 2 to about 8 carbon atoms, alkynyl having 2 to about 8 carbon atoms, cyano, nitro, etc.;

n is an integer of from 0 (where the ring is fully hydrogen-substituted) to 7, and preferably n is 0, 1 or 2.

x' is the mole fraction or percent of alkyl acrylate units in the polymer and preferably is from 10 to about 80 percent; and y' is the mole fraction or percent of quinolinyl or hydroxyquinolinyl units in the polymer and preferably is from about 5 to about 90 percent. The polymer also may contain other units if desired, but preferably the polymer will contain at least about 10 mole percent of quinolinyl and/or hydroxyquinolinyl units. Hydroxyalkyl is a particularly preferred R^6 group, especially alkyl having a primary hydroxy group such as where R^6 is 2-hydroxyethylene.

The above-mentioned substituted groups (i.e. substituted groups R^1 through R^7 and W) may be substituted at one or more available positions by one or more suitable groups such as e.g. halogen (particularly F, Cl and Br); cyano; hydroxyl, nitro, alkanoyl such as a C_{1-6} alkanoyl group such as acyl and the like; alkyl groups having from 1 to about 8 carbon atoms; alkenyl and alkynyl groups having one or more unsaturated linkages and 2 to about 8 carbon atoms; alkoxy groups having from 1 to about 6 carbons; etc.

As discussed above, the ARC resin binders are preferably synthesized by polymerizing two or more different monomers where at least one of the monomers includes a chromophore group, e.g. an anthracenyl, quinolinyl or hydroxyquinolinyl group. A free radical polymerization is suitably employed, e.g., by reaction of a plurality of monomers to provide the various units in the presence of a radical initiator preferably under an inert atmosphere (e.g., N_2 or argon) and at elevated temperatures such as about 70° C. or greater, although reaction temperatures may vary depending on the reactivity of the particular reagents employed and the boiling point of the reaction solvent (if a solvent is employed). See the examples which follow for exemplary reaction conditions. Suitable reaction temperatures for any particular system can be readily determined empirically by those skilled in the art based on the present disclosure. A reaction solvent may be employed if desired. Suitable solvents include alcohols such as propanols and butanols and aromatic solvents such as benzene, chlorobenzene, toluene and xylene. Dimethylsulfoxide, dimethylformamide and THF are also suitable. The polymerization reaction also may be run neat. A variety of free radical initiators may be employed to prepare the copolymers of the invention. For example, azo compounds may be employed such as azo-bis-2,2'-isobutyronitrile (AIBN) and 1,1'-azobis(cyclohexanecarbonitrile). Peroxides, peresters, peracids and persulfates also can be employed.

Also, while less preferred, a preformed resin may be functionalized with chromophore units. For example, a glycidyl phenolic resin such as a glycidyl novolac can be reacted with an anthranyl carboxylic acid.

Preferably the ARC resin binder will have a weight average molecular weight (Mw) of about 1,000 to about 10,000,000 daltons, more typically about 5,000 to about

1,000,000 daltons, and a molecular number molecular weight (Mn) of about 500 to about 1,000,000 daltons. Molecular weights (either Mw or Mn) of the polymers of the invention are suitably determined by gel permeation chromatography.
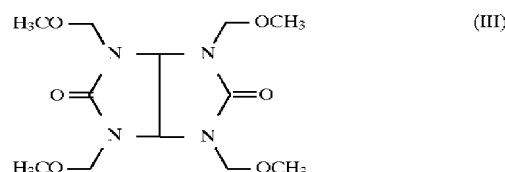
Resin binders of the invention preferably exhibit good absorbance at deep UV wavelengths such as within the range of from 100 to about 300 nm. More specifically, preferred resin binders of the invention have optical densities of at least about 3 absorbance units per micron (Absorb. units/μ) at about 248 nm, preferably from about 5 to 20 or more absorbance units per micron at 248 nm, more preferably from about 8 to 16 or more absorbance units per micron at 248 nm. Higher absorbance values for a particular resin can be obtained by increasing the percentage of chromophore units on the resin.

The antireflective compositions of the invention also may contain resins that do not include polycyclic chromophore units as a co-resin present with resins having polycyclic chromophore units, or as the sole resin of the ARC binder component. For example, phenolic resins such as the poly (vinylphenols), novolaks and other resins described below as photoresist resin binders could be employed in resin binder components of ARCs of the invention.

The concentration of the resin binder component of the antireflective compositions of the invention may vary within relatively broad ranges, and in general the resin binder is employed in a concentration of from about 50 to 95 weight percent of the total of the dry components of the ARC, more typically from about 60 to 90 weight percent of the total dry components (all components except solvent carrier).

ARCs of the invention also contain a crosslinker component. A variety of crosslinkers may be employed, including those ARC crosslinkers disclosed in the above-mentioned Shipley European Application 542008.

Low basicity crosslinkers are particularly preferred such as a methoxy methylated glycouril. A specifically preferred crosslinker is a methoxy methylated glycouril corresponding to the following structure (III):

(III)

This methoxy methylated glycouril can be prepared by known procedures. The compound is also commercially available under the tradename of Powderlink 1174 from the American Cyanamid Co.

Other suitable low basicity crosslinkers include hydroxy compounds, particularly polyfunctional compounds such as phenyl or other aromatics having one or more hydroxy or hydroxy alkyl substituents such as a C_{1-8} hydroxyalkyl substituents. Phenol compounds are generally preferred such as di-methanolphenol ($C_6H_3(CH_2OH)_2OH$) and other compounds having adjacent (within 1–2 ring atoms) hydroxy and hydroxyalkyl substitution, particularly phenyl or other aromatic compounds having one or more methanol or other hydroxylalkyl ring substituent and at least one hydroxy adjacent such hydroxyalkyl substituent.

It has been found that a low basicity crosslinker such as a methoxy methylated glycouril used in antireflective compositions of the invention can provide excellent lithographic performance properties, including the substantial reduction or even elimination (SEM examination) of undercutting or footing of an overcoated photoresist relief image.

The antireflective compositions of the invention preferably further comprise an acid or acid generator compound for catalyzing or promoting reaction of the glycouril compound during curing of an ARC coating layer. Preferably an acid generator compound is employed that liberates acid upon photolysis or thermal treatment. Preferably a thermal acid generator is employed, i.e. a compound that generates acid upon thermal treatment. A variety of known thermal acid generators are suitably employed such as e.g. 2,4,4,6-tetrabromocyclohexadienone, benzoin tosylate, 2-nitrobenzyl tosylate and other alkyl esters of organic sulfonic acids. Compounds that generate a sulfonic acid upon activation are generally suitable. Typically a thermal acid generator is present in an antireflective composition in concentration of from about 0.5 to 15 percent by weight of the total of the dry components of the composition, more preferably about 2 percent by weight of the total dry components. Photoacid generators also may be employed in an antireflective composition, for example onium salts, halogenated non-ionic photoacid generators such as 1,1-bis [p-chlorophenyl]-2,2,2-trichloroethane, and other photoacid generators disclosed herein for use in photoresist compositions. Suitable amounts of a photoacid generator in an antireflective composition in general range from about 1 to 15 percent by weight of the total of dry components of the composition. For an antireflective composition containing a photoacid generator, a coating layer of the composition is exposed to an effective amount of activating radiation to generate the photoacid, followed by a post-exposure bake at a temperature sufficient to cure the coating layer. However, in generally preferred embodiments of the invention an antireflective composition is completely or at least essentially free (e.g., less than about 1 weight percent based on total dry components weights) of a photoacid generator, and an acid or thermal acid generator is used as an acid source and the ARC is cured thermally without an exposure step.

Also, as discussed above, rather than an acid generator, an acid may be simply formulated into the ARC, particularly for ARCs that require heating to cure in the presence of acid so that the acid does not promote undesired reaction of composition components prior to use of the ARC. Suitable acids include e.g. strong acids such as sulfonic acids such as toluene sulfonic acid and sulfonic acid, triflic acid, or mixtures of those materials.

Antireflective compositions of the invention also may contain additional dye compounds that absorb radiation used to expose an overcoated photoresist layer. Other optional additives include surface leveling agents, for example, the leveling agent available under the tradename Silwet 7604 from Union Carbide, or the surfactant FC 171 available from the 3M Company.

To make a liquid coating composition, the components of the antireflective composition are dissolved in a suitable solvent such as, for example, ethyl lactate or one or more of the glycol ethers such as 2-methoxyethyl ether (diglyme), ethylene glycol monomethyl ether, and propylene glycol monomethyl ether; solvents that have both ether and hydroxy moieties such as methoxy butanol, ethoxy butanol, methoxy propanol and ethoxy propanol; esters such as methyl cellosolve acetate, ethyl cellosolve acetate, propylene glycol monomethyl ether acetate, dipropylene glycol monomethyl ether acetate and other solvents such as dibasic esters, propylene carbonate and gamma-butyro lactone. The concentration of the dry components in the solvent will depend on several factors such as the method of application. In general, the solids content of an antireflective composition varies from about 0.5 to 20 weight percent of the total weight of the antireflective composition, preferably the

solids content varies from about 2 to 10 weight percent of the total weight of the antireflective composition.

A variety of photoresist compositions can be employed with the antireflective compositions of the invention, including positive-acting and negative-acting photoacid-generating compositions. Photoresists of the invention typically comprise a resin binder and a photoactive component, typically a photoacid generator compound. Preferably the photoresist resin binder has finctional groups that impart alkaline aqueous developability to the images resist composition. Preferred are resin binders that comprise polar functional groups such as hydroxyl or carboxylate and the resin binder is used in a resist composition in an amount sufficient to render the resist developable with an aqueous alkaline solution.

Generally preferred resist resin binders are phenolic resins including phenol aldehyde condensates known in the art as novolak resins, homo and copolymers or alkenyl phenols and homo and copolymers of N-hydroxyphenyl-maleimides.

Examples of suitable phenols for condensation with a aldehyde, especially formaldehyde, for the formation of novolak resins include phenol; m-cresol; o-cresol; p-cresol; 2,4-xylenol; 2,5-xylenol; 3,4-xylenol; 3,5-xylenol; thymol and mixtures thereof. An acid catalyzed condensation reaction results in formation of a suitable novolak resin which may vary in molecular weight (Mw) from about 500 to 100,000 daltons. Poly(vinylphenols) may be prepared, e.g., as disclosed in U.S. Pat. No. 4,439,516. Preferred resin binders and the preparation thereof are also disclosed in U.S. Pat. No. 5,128,230.

Poly(vinylphenols) may be formed by block polymerization, emulsion polymerization or solution polymerization of the corresponding monomers in the presence of a catalyst. Vinylphenols useful for the production of polyvinyl phenol resins may be prepared, for example, by hydrolysis of commercially available coumarin or substituted coumarin, followed by decarboxylation of the resulting hydroxy cinnamic acids. Useful vinylphenols also may be prepared by dehydration of the corresponding hydroxy alkyl phenols or by decarboxylation of hydroxy cinnamic acids resulting from the reaction of substituted or nonsubstituted hydroxybenzaldehydes with malonic acid. Preferred polyvinylphenol resins prepared from such vinylphenols have a molecular weight (Mw) range of from about 2,000 to about 60,000 daltons.
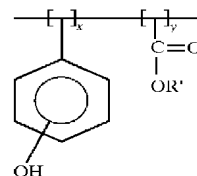
Copolymers containing phenol and nonaromatic cyclic alcohol units also are preferred resin binders for resists of the invention and may be suitably prepared by partial hydrogenation of a novolak or poly(vinylphenol) resin. Such copolymers and the use thereof in photoresist compositions are disclosed in U.S. Pat. No. 5,128,232 to Thackeray et al.

Further preferred resin binders include resins formed from bishydroxymethylated compounds, and block novolak resins. See U.S. Pat. Nos. 5,130,410 and 5,128,230 where such resins and use of same in photoresist compositions is disclosed. Additionally, two or more resin binders of similar or different compositions can be blended or combined together to give additive control of lithographic properties of a photoresist composition. For instance, blends of resins can be used to adjust photospeed and thermal properties and to control dissolution behavior of a resist in a developer.

One suitable class of photoresists for use with ARCs of the invention are "conventional" positive-acting resists that comprise a photoacid generator and a resin binder component such as a novolak or poly(vinylphenol) or partially hydrogenated derivative thereof and wherein the photoactive component serves as a dissolution rate inhibitor. Pho-

toactivation of a coating layer of the resist results in conversion of the photoactive component to an acidic material, rendering regions of the coating layer containing this acidic photoproduct comparatively more soluble in an aqueous alkaline developer solution than regions that contain only the intact (non-activated) photoactive component. The photoactive component typically used in these positive resists are quinone diazides such as 2,1,4-diazonaphthoquinone sulfonic acid esters and 2,1,5-diazonaphthoquinone sulfonic acid esters.

In particularly preferred aspects of the invention, the ARCs of the invention are used with chemically amplified positive-acting resist compositions. A number of such resist compositions have been described, e.g., in U.S. Pat. Nos. 4,968,581; 4,883,740; 4,810,613 and 4,491,628, all of which are incorporated herein by reference for their teaching of making and using chemically amplified positive-acting resists. A particularly preferred chemically amplified photoresist for use with an ARC of the invention comprises in admixture a photoacid generator and a resin binder that comprises a copolymer containing both phenolic and non-phenolic units. For example, one preferred group of such copolymers has acid labile groups substantially, essentially or completely only on non-phenolic units of the copolymer. One especially preferred copolymer binder has repeating units x and y of the following formula:

wherein the hydroxyl group be present at either the ortho, meta or para positions throughout the copolymer, and R' is substituted or unsubstituted alkyl having 1 to about 18 carbon atoms, more typically 1 to about 6 to 8 carbon atoms. Tert-butyl is a generally preferred R' group. An R' group may be optionally substituted by e.g. one or more halogen (particularly F, Cl or Br), C_{1-8} alkoxy, C_{2-8} alkenyl, etc. The units x and y may be regularly alternating in the copolymer, or may be randomly interspersed through the polymer. Such copolymers can be readily formed. For example, for resins of the above formula, vinyl phenols and a substituted or unsubstituted alkyl acrylate such as t-butylacrylate and the like may be condensed under free radical conditions as known in the art. The substituted ester moiety, i.e. R'—O—C(=O)—, moiety of the acrylate units serves as the acid labile groups of the resin and will undergo photoacid induced cleavage upon exposure of a coating layer of a photoresist containing the resin. Preferably the copolymer will have a Mw of from about 8,000 to about 50,000, more preferably about 15,000 to about 30,000 with a molecular weight distribution of about 3 or less, more preferably a molecular weight distribution of about 2 or less. Non-phenolic resins, e.g. a copolymer of an alkyl acrylate such as t-butylacrylate or t-butylmethacrylate and a vinyl alicyclic such as a vinyl norbornyl or vinyl cyclohexanol compound, also may be used as a resin binder in compositions of the invention. Such copolymers also may be prepared by such free radical polymerization or other known procedures and suitably will have a Mw of from about 8,000 to about 50,000, and a molecular weight distribution of about 3 or less. Additional preferred chemically-amplified positive resists are disclosed in U.S. Pat. No. 5,258,257 to Sinta et al.

Preferred negative-acting resist compositions for use with an ARC of the invention comprise a mixture of materials that will cure, crosslink or harden upon exposure to acid, and a photoacid generator.

Particularly preferred negative-acting resist compositions comprise a resin binder such as a phenolic resin, a crosslinker component and a photoactive component of the invention. Such compositions and the use thereof have been disclosed in European Patent Applications 0164248 and 0232972 and in U.S. Pat. No. 5,128,232 to Thackeray et al. Preferred phenolic resins for use as the resin binder component include novolaks and poly(vinylphenol)s such as those discussed above. Preferred crosslinkers include amine-based materials, including melamine, glycourils, benzoguanamine-based materials and urea-based materials. Melamine-formaldehyde resins are generally most preferred. Such crosslinkers are commercially available, e.g. the melamine resins sold by American Cyanamid under the trade names Cymel 300, 301 and 303. Glycouril resins are sold by American Cyanamid under trade names Cymel 1170, 1171, 1172, Powderlink 1174, urea-based resins are sold under the trade names of Beetle 60, 65 and 80, and benzoguanamine resins are sold under the trade names Cymel 1123 and 1125.

Suitable photoacid generator compounds of resists used with ARCs of the invention include the onium salts, such as those disclosed in U.S. Pat. Nos. 4,442,197, 4,603,101, and 4,624,912, each incorporated herein by reference; and non-ionic organic photoactive compounds such as the halogenated photoactive compounds as in U.S. Pat. No. 5,128,232 to Thackeray et al. and sulfonate photoacid generators including sulfonated esters and sulfonyloxy ketones. See *J. of Photopolymer Science and Technology*, 4(3):337–340 (1991), for disclosure of suitable sulfonate PAGS, including benzoin tosylate, t-butylphenyl alpha-(p-toluenesulfonyloxy)-acetate and t-butyl alpha-(p-toluenesulfonyloxy)-acetate. Preferred sulfonate PAGs are also disclosed in U.S. Pat. No. 5,344,742 to Sinta et al.

Photoresists for use with an ARC of the invention also may contain other materials. For example, other optional additives include actinic and contrast dyes, anti-striation agents, plasticizers, speed enhancers, etc. Such optional additives typically will be present in minor concentration in a photoresist composition except for fillers and dyes which may be present in relatively large concentrations such as, e.g., in amounts of from 5 to 30 percent by weight of the total weight of a resist's dry components.

ARCs of the invention that include a low basicity crosslinker such as a suitable glycouril are particularly useful with photoresists that generate a strong acid photoproduct upon exposure such as triflic acid, camphor sulfonate or other sulfonic acid, or other acid having a pKa (25° C.) of about 2 or less. Without wishing to be bound by theory, it is believed ARCs of the invention are particularly effective with such strong acid resists because the strong photogenerated acid will migrate from the resist and remain in the ARC layer to a lesser extent relative to a comparable ARC that contain a more basic crosslinker. That is, the low basicity crosslinkers of the invention will tie up strong photogenerated acids of an overcoated resist layer to a lesser extent than a more basic ARC crosslinker. As a result thereof, less acid loss from the resist layer will occur and resolution problems such as footing will be reduced.

In use, an antireflective composition of the invention is applied as a coating layer to a substrate may any of a variety of methods such as spin coating. The antireflective composition in general is applied on a substrate with a dried layer

thickness of between about 0.02 and 0.5 μm, preferably a dried layer thickness of 5 between about 0.04 and 0.20 μm. The substrate is suitably any substrate conventionally used in processes involving photoresists. For example, the substrate can be silicon, silicon dioxide or aluminum-aluminum oxide microelectronic wafers. Gallium arsenide, ceramic. quartz or copper substrates may also be employed. Substrates used for liquid crystal display or other flat panel display applications are also suitably employed, for example glass substrates, indium tin oxide coated substrates and the like.

Preferably the antireflective layer is cured before a photoresist composition is applied over the ARC. Cure conditions will vary with the components of the ARC. Thus, if the composition does not contain an acid or acid generator, cure temperatures and conditions will be more vigorous than those of a composition containing an acid or acid generator compound. Typical cure conditions are from about 120° C. to 225° C. for about 0.5 to 40 minutes. Cure conditions preferably render the ARC coating layer substantially insoluble to the photoresist solvent as well as an alkaline aqueous developer solution. Additionally, as discussed above, if the ARC includes a photoacid generator, the composition coating layer can be at least partially cured by exposing the coating layer to an effective amount of activating radiation (e.g., between about 10 to 300 mJ/cm^2), followed by a post-exposure bake of from 50° to 225° C.

After such curing a photoresist is applied over the surface of the ARC. As with application of the ARC, the photoresist can be applied by any standard means such as by spinning, dipping, meniscus or roller coating. Following application, the photoresist coating layer is typically dried by heating to remove solvent preferably until the resist layer is tack free. Optimally, essentially no intermixing of the ARC layer and photoresist layer should occur.

The resist layer is then imaged with activating radiation through a mask in conventional manner. The exposure energy is sufficient to effectively activate the photoactive component of the resist system to produce a patterned image in the resist coating layer, more specifically, the exposure energy typically ranges from about 3 to 300 mJ/cm^2 depending upon the exposure tool. The exposed resist layer may be subjected to a post-exposure bake if desired to create or enhance solubility differences between exposed and unexposed regions of a coating layer. For example, negative acid-hardening photoresists typically require post-exposure heating to induce the acid-promoted crosslinking reaction, and many chemically amplified positive-acting resists require post-exposure heating to induce an acid-promoted deprotection reaction. Typically post-exposure bake conditions include temperatures of about 50° C. or greater, more specifically a temperature in the range of from about 50° C. to 160° C.

The exposed resist coating layer is then developed, preferably with an aqueous based developer such as an inorganic alkali exemplified by tetrabutyl ammonium hydroxide, sodium hydroxide, potassium hydroxide, sodium carbonate, sodium bicarbonate, sodium silicate, sodium metasilicate, aqueous ammonia or the like. Alternatively, organic developers can be used. In general, development is in accordance with art recognized procedures. Following development, a final bake of an acid-hardening photoresist is often employed at temperatures of from about 100° to 150° C. for several minutes to further cure the developed exposed coating layer areas.

The developed substrate may then be selectively processed on those substrates areas bared of photoresist, for

example chemically etching or plating substrate areas bared of photoresist in accordance with procedures well known in the art. Suitable etchants include a hydrofluoric acid etching solution and a plasma gas etch such as an oxygen plasma etch. A plasma gas etch removes the crosslinked antihalation coating layer.

All documents mentioned herein are incorporated herein by reference.

The following non-limiting examples are illustrative of the invention.

EXAMPLES 1–6

Preparation of preferred ARC resin binders.
1. Preparation of monomers with chromophores.
   A. Preparation of chloroxine methacrylate.

A 500 ml round bottom flask equipped with magnetic stirrer and nitrogen inlet was charged with 5.0 g (0.0234 mol) 5.7 dichloro-8-hydroxyquinoline (chloroxine), 2.01 (0.0234 mol) methacrylic acid, 500 ml methylene chloride, 1.43 g (0.5 eq.), 4-dimethylamino-pyridine (DMAP) and 6.72 g 1-(3-dimethylamino propyl)-3-ethylcarbodimide (EDCI). The reaction mixture was stirred under a blanket of nitrogen for 12 hours at 25° C. The product was purified by column chromatography (methylene chloride) to give a pale yellow solid (yield 67%).

B. Preparation of methylanthracene methacrylate.

Methylanthracene methacrylate ($CH_3C(=CH_2)CO_2CH_2$-9-anthracene) was prepared as disclosed in *Macromolecules*, 17(2):235 (1984).
2. Preparation of resins.

Hydroxyethyl methacrylate (HEMA)/methylanthracene methacrylate (ANTMA) copolymer (Formula II above) was prepared as follows.

A 300 ml 3N round bottom flask equipped with magnetic stirrer, condenser, nitrogen and vacuum inlet was charged with 16.0 g (0.1229 mol) HEMA (purified by distillation), 8.49 g (0.0307 mol) methylanthracene methacrylate, 0.2449 g (1 wt. %) AIBN and 180 ml THF. The reaction flask was quenched in liquid nitrogen while being purged with nitrogen. When the contents of the reaction flask were frozen, the flask was evacuated, then purged with nitrogen (3 times). The reaction mixture was stirred under reflux for 18 hours. The pale yellow polymer was precipitated into 3000 ml ether, filtered, then dried at 50° C. under vacuum (yield 86%) to provide the HEMA/ANTMA copolymer having 81 mole percent of $-CH_2C(CH_3)(CO_2CH_2CH_2OH)-$ units and 19 mole percent of $-CH_2C(CH_3)(CO_2CH_2-9-$ anthracene) units, a Mn of 2295, Mw of 19150 and a Tg of 101° C.

Additional HEMA/ANTMA copolymers and HEMA/ chloroxine methacrylate copolymers (resins of Examples 2–6) were prepared by similar procedures, with the substitution of chloroxine methacrylate for methylanthracene methacrylate in the case of preparation of HEMA/chloroxine methacrylate copolymers.

EXAMPLES 7–14

Preparation and use of ARCs of the invention.

EXAMPLE 7

A preferred antireflective composition of the invention was prepared by mixing the components set forth below, with component amounts expressed as parts by weight based on total weight of the liquid antireflective coating composition:

1) Resin binder: 2.33% Polymer (novolac resin base with approximately 4% glycidyl groups replacing OH, and approximately 80% of OH groups replaced by $-O(C=O)CH_2$9-anthracene)
2) Crosslinker: 0.61% Powderlink 1174 (American Cyanamid)
3) Acid: 0.06% p-toluene sulfonic acid
4) Solvent: 18% ethyl lactate; 10% cyclohexanone; and 68.97% propylene glycol monomethyl ether

The antireflective composition was spin coated onto a single crystal silicon substrate 100 mm in diameter at 3100 rpm, and baked on a vacuum hot plate at 205° C. for 60 seconds. The resulting thickness was 600 angstroms. Over this ARC layer a commercially available DUV negative photoresist (sold under the tradename of CGR248 and available from IBM) was applied to a thickness of 8900 Å after a vacuum hot plate bake at 95° C. for 60 seconds. The overcoated resist layer was exposed to KrF excimer radiation (248nm) with an ISI XLS projection stepper through a mask patterned with small lines and spaces with a dose of 9 mJ/cm². The wafer was then baked on a vacuum hot plate at 95° C. for 60 seconds, and then developed with MF702 developer (Shipley Co.; alkaline aqueous solution) for 40 seconds. Resist footing was measured by cross-section SEMs for both isolated and dense lines 0.27 μm wide and averaged 12 nm.

EXAMPLE 8

A further preferred antireflective composition of the invention was prepared by mixing the components set forth below, with component amounts expressed as parts by weight based on total solids (all components except solvent) of the antireflective coating composition:
1) Resin binder: 2.33% Polymer (novolac resin base with ~4% glycidyl groups replacing OH, and ~80% of OH groups replaced by $-O(C=O)CH_2$9-anthracene)
2) Crosslinker: 0.61% Powderlink 1174 (American Cyanamid)
3) Acid: 0.06% p-toluene sulfonic acid
4) Surfactant: 0.03% FC 171 (3M Co.)
5) Solvent: 18% ethyl lactate; 10% cyclohexanone; and 68.97% propylene glycol monomethyl ether

This antireflective composition was spin coated onto a single crystal silicon substrate 100 mm in diameter, and baked on a vacuum hot plate at 205° C. for 60 seconds. The resulting thickness was 600 Å. Over this ARC layer a coating layer of a DUV negative photoresist was applied. The resist contained (amounts expressed in weight percents): 88.34% 12% mesylated poly(vinylphenol) (Mw= 5000); 2.65% triarylsulfonium triflate; 8.83% Powderlink 1174; 0.177% tetrabutylammonium hydroxide; 0.2% Silwet 7604; and solvent of ethyl lactate to a thickness of 7575 Å after a vacuum hot plate bake at 90° C. for 60 seconds. Preparation of mesylated poly(vinylphenol) is described in U.S. Pat. No. 5,514,520 issued on May 7, 1996. The overcoated resist was exposed to KrF excimer radiation (248 nm) with an ISI XLS projection stepper through a mask patterned with small lines and spaces with a dose of 17.9 mJ/cm₂. The wafer was then baked on a vacuum hot plate at 130° C. for 60 seconds, and then developed with CD26 (Shipley) developer for 35 seconds. Resist footing was measured by cross-section SEMs for both isolated and dense lines 0.25 um wide and averaged 6 nm.

EXAMPLE 9

A further preferred antireflective composition of the invention was prepared by mixing the components set forth

below, with component amounts expressed as parts by weight based on total weight of the liquid antireflective coating composition:

1) Resin binder: 2.62% copolymer of 9-anthrylmethylmethacrylate (26mol %) and 2-hydroxyethylmethacrylate (74 mol %)
2) Crosslinker: 0.36% Powderlink 1174 (American Cyanamid)
3) Thermal Acid Crosslinker: 0.02% 2-nitrobenzyltosylate
4) Surfactant: 0.003% FC431 (fluorinated alkyl ester available from 3M Co.)
5) Solvent: 96% propylene glycol monomethyl ether; 1.0% cyclohexanone

This antireflective composition was spincoated onto a single crystal silicon substrate 100 mm in diameter, and baked on a vacuum hot plate at 150° C. for 60 seconds. The resulting coating layer thickness of the ARC was 740 Å. Over this ARC a commercially available DUV positive photoresist (sold under the tradename UVIIHS and available from the Shipley Co.) was applied to a thickness of 8900 Å after a vacuum hot plate bake at 140° C. for 60 seconds. It was exposed to KrF excimer radiation (248 nm) with an ISI XLS projection stepper through a mask patterned with small lines and spaces with a dose of 11.0 mJ/cm$_2$. The wafer was then baked on a vacuum hot plate at 135° C. for 90 seconds, and then developed with CD26 (Shipley) developer for 50 seconds. Resist footing was measured by cross section SEMs for both isolated and dense lines.

EXAMPLE 10

A further preferred antireflective composition was prepared by mixing the following components, with component amounts expressed as parts by weight based on total weight of the liquid antireflective composition:

1) Resin binder: 3.88% Polymer (novolac resin base with ~4% glycidyl groups replacing OH, and ~80% of OH groups replaced by —O(C=O)CH$_2$-9-anthracene+~10% residual 9-anthracene carboxylic acid)
2) Crosslinker: 1.02% Powderlink 1174 (American Cyanamid)
3) Acid: 0.10% p-toluene sulfonic acid
4) Surfactant: 0.05% FC 171 (3M Co)
5) Solvent: 94.97% propylene glycol monomethyl ether

This ARC was spin coated onto a single crystal silicon substrate 100 mm in diameter, and baked on a vacuum hot plate at 205° C. for 60 seconds. The resulting thickness was 988 Å. Over this was coated a commercial DLIV positive photoresist, UVIIIS (Shipley Co.) to a thickness of 8620A after a vacuum hot plate baked at 140° C. for 60 seconds. It was exposed to KrF excimer radiation (248 nm) with an ISI XLS projection stepper through a mask patterned with small lines and spaces with a dose of 11.0 mJ/cm^2. The wafer was then baked on a vacuum hot plate at 140° C. for 90s, and then developed with CD26 (Shipley) developer for 50 seconds. Resist footing was measured by cross-section SEMs for both isolated and dense lines 0.25μm wide and averaged~4nm.

EXAMPLE 11

A further preferred antireflective composition was prepared by mixing the following components, with component amounts expressed as parts by weight based on total weight of the liquid antireflective composition:

1) Resin binder: 3.88% Polymer (novolac resin base with~4% glycidyl groups replacing OH, and ~45% of OH groups replaced by —O(C=O)CH$_2$—9-anthracene and

35% of OH groups replaced by COHCH$_2$O(C=O)CH$_3$+ ~7% residual 9-anthracene carboxylic acid)
2) Crosslinker: 1.02% Powderlink 1174 (American Cyanamid)
3) Acid: 0.10% p-toluene sulfonic acid
4) Surfactant: 0.05% FC 171 (3M Co)
5) Solvent: 94.97% propylene glycol monomethyl ether

This ARC was spin coated onto a single crystal silicon substrate 100 mm in diameter, and baked on a vacuum hot plate at 205° C. for 60 seconds. The resulting thickness was 1095 Å. Over this was coated a commercial DUV positive photoresist, APEX-E (Shipley Co.) to a thickness of 8394 A after a vacuum hot plate baked at 90° C. for 60 seconds. It was exposed to KrF excimer radiation (248 um) with an ISI XLS projection stepper through a mask patterned with small lines and spaces with a dose of 8.6 mJ/cm^2. The wafer was then baked on a vacuum hot plate at 90° C. for 60s, and then developed with MF702 (Shipley) developer for 60 seconds. Resist footing was measured by cross-section SEMs for both isolated and dense lines 0.30 μm wide and averaged ~5 nm.

EXAMPLE 12

A further preferred antireflective composition was prepared by mixing the following components, with component amounts expressed as parts by weight based on total weight of the liquid antireflective composition: A solution containing:

1) Resin binder: 2.58% terpolymer of 9-anthrylmethylmethacrylate (24 mol %), 2-hydroxyethylmethacrylate (54 mol %) and methacrylic acid (22%)
2) Crosslinker: 0.38% Powderlink 1174 (American Cyanamid)
3) Thermal Acid Crosslinker: 0.038% benzoin tosylate
4) Surfactant: 0.003% FC431 (3M Co)
5) Solvent: 97% propylene glycol monomethyl ether

This ARC was spin coated onto a single crystal silicon substrate 100 mm in diameter, and baked on a vacuum hot plate at 175° C. for 60 seconds. The resulting thickness was 595 Å. Over this was coated a commercial DUV positive photoresist, UVIIHS (Shipley Co.) to a thickness of 7950A after a vacuum hot plate baked at 135° C. for 60 seconds. It was exposed to KrF excimer radiation (248 nm) with an ISI XLS projection stepper. The wafer was then baked on a vacuum hot plate at 130° C. for 60 seconds, and then developed with CD26 (Shipley) developer for 50 seconds. Resist footing was measured by cross-section SEMs for both isolated and dense lines 0.25 μm wide and averaged ~19 nm.

EXAMPLE 13

A further preferred antireflective composition was prepared by mixing the following components, with component amounts expressed as parts by weight based on total weight of the liquid antireflective composition:

1) Resin binder: 3.58% copolymer: methylmethacrylate (39 mol %), 2-hydroxyethylmethacrylate (27%), methacrylic acid (7%) and butyl acrylate (27%)
2) Crosslinker: 1.0% Powderlink 1174 (American Cyanamid)
3) Thermal Acid Generator: 0.0185% 2-nitrobenzyltosylate
4) Surfactant: 0.002% Silwet L7001 (Union Carbide)
5) Solvent: 95% propylene glycol monomethyl ether

This ARC was spin coated onto a single crystal silicon substrate 100 mm in diameter, and baked on a vacuum hot plate at 150° C. for 60 seconds. The resulting thickness was 1180 Å. Over this was coated a commercial DUV positive

photoresist, APEX-E (Shipley Co.) to a thickness of 8400 A after a vacuum hot plate baked at 90° C. for 60 seconds. It was exposed to KrF excimer radiation (248 mn) with an ISI XLS projection stepper through a mask patterned with small lines and spaces with a dose of 6.0 mJ/cm². The wafer was then baked on a vacuum hot plate at 90° C. for 90s, and then developed with MF321 (Shipley) developer for 60 seconds. Resist footing was measured by cross-section SEMs for both isolated and dense lines 0.30 μm wide and averaged 43 μm.

EXAMPLE 14

A further preferred antireflective composition was prepared by mixing the following components, with component amounts expressed as parts by weight based on total weight of the liquid antireflective composition:

1) Resin binder: 3.8% copolymer of 9-anthrylmethylmethacrylate (32 mol%) and 2-hydroxyethylmethacrylate (68 mol %)
2) Crosslinker: 1.0% Powderlink 1174 (American Cyanamid)
3) Thermal Acid Generator: 0.185% 2-nitrobenzyltosylate
4) Surfactant: 0.0015% FC431 (3M Co.)
5) Solvent: 95% propylene glycol monomethyl ether

This ARC was spin coated onto a single crystal silicon substrate 100 mm in diameter, and baked on a vacuum hot plate at 150° C. for 60 seconds. The resulting thickness was 1077 Å. Over this was coated a commercial DUV positive photoresist, APEX-E (Shipley Co.) to a thickness of 8400 A after a vacuum hot plate baked at 90° C. for 60 seconds. It was exposed to KrF excimer radiation (248 nm) with an ISI XLS projection stepper through a mask patterned with small lines and spaces with a dose of 7.3 'mJ/cm². The wafer was then baked on a vacuum hot plate at 90° C. for 90s, and then developed with MF321 (Shipley) developer for 60 seconds. Resist footing was measured by cross-section SEMs for both isolated and dense lines 0.30 μm wide and averaged 12 nm.

The foregoing description of the invention is merely illustrative thereof, and it is understood that variations and modifications can be effected without departing from the scope or spirit of the invention as set forth in the following claims.

What is claimed is:

1. An antireflective coating composition for use with an overcoated photoresist composition, the antireflective composition comprising a crosslinker and a resin binder comprises a polymer corresponding to the following formula:

wherein each R and R^1 is independently hydrogen or a substituted or unsubstituted alkyl group having from 1 to about 8 carbon atoms;

each R^2 is independently substituted or unsubstituted alkyl having 1 to about 10 carbon atoms;

each R^3 is independently halogen, alkyl having 1 to about 8 carbon atoms, alkoxy having 1 to about 8 carbon atoms, alkenyl having 2 to about 8 carbon atoms, alkynyl having 2 to about 8 carbon atoms, cyano, or nitro;

m is an integer of from 0 to 9; and

x is from about 10 to about 80 percent; and y is from about 5 to 90 percent.

2. The antireflective composition of claim 1 wherein R^2 is a hydroxyalkyl.

3. The antireflective composition of claim 1 wherein the sum of x and y is about 100 percent.

4. The antireflective composition of claim 1 wherein the crosslinker is a methoxy methylated glycouril.

5. The antireflective composition of claim 1 wherein the crosslinker compound has the following structure:

6. The antireflective composition of claim 1 wherein the crosslinker is a polyhydroxy compound.

7. The antireflective composition of claim 6 wherein the crosslinker is an aromatic compound with at least one hydroxy and at least one hydroxy alkyl substituent.

8. The antireflective composition of claim 1 further comprising an acid or acid generator compound.

9. An antireflective coating composition for use with an overcoated photoresist composition, the antireflective composition comprising a crosslinker and a resin binder comprises a polymer of the following structure:

wherein x and y are mole fractions of the respective units.

* * * * *

United States Patent [19]

Petersen et al.

[54] **ANTIREFLECTIVE COATING PROCESS**

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[73] Assignees: **Shipley Company, L.L.C.**, Marlboro, Mass.; **Sematech, Inc.**, Austin, Tex.

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M. Bolsen, et al.; "One Micron Lithography Using a Dyed Resist on Highly Reflective Topography", *Solid State Technology*, Feb. 1986.

[57] **ABSTRACT**

Reduction of reflection from an integrated circuit substrate during exposure of a photoresist layer on a surface such as an integrated circuit wafer is minimized by incorporating an antireflective coating between the photoresist layer and the integrated circuit substrate. The antireflective layer, after exposure and development of the photoresist layer, is preferably removed by exposing the non-masked antireflective layer to activating radiation while heating the coating to induce a solubilizing reaction in an antireflective coating and a curing reaction in an overlying photoresist mask. Thereafter, the exposed portions of the antireflective layer are removed by treatment with a suitable developer.

22 Claims, No Drawings

ANTIREFLECTIVE COATING PROCESS

BACKGROUND OF THE INVENTION

I. Introduction

This invention relates to reduction of reflection from a substrate surface during the processing of photoresists in integrated circuit manufacture. More particularly, this invention relates to antireflective coatings (ARC's) and a simplified process for use and removal of the same to provide an image of enhanced resolution.

II. Description of the Prior Art

It is known in the art that during the manufacture of integrated circuits, silicon wafers are coated with photoresist, exposed to activating radiation, and developed to define a relief image over the wafer surface. The relief image defines open areas over the substrate in a desired image pattern to be transferred to a substrate. The image is transferred to the surface of the substrate by surface modification of the substrate in a negative image of the pattern within the photoresist coating, such as by removal of a portion of the substrate surface by an etching process or by implantation of an atomic species into the substrate surface. During these processes, the coating of the photoresist in the image pattern functions as a protective mask to prevent surface modification of the substrate underlying the photoresist mask. The resolution of the image transferred to the substrate is dependent upon the resolution within the imaged photoresist coating.

There are factors in addition to the resolution capability of the photoresist used that influence the quality or resolution of the image transferred to a photoresist masked substrate. For example, with reflective integrated circuit substrates, such as aluminum, exposure of a photoresist coating causes reflection of diffused activating radiation (light) from the integrated circuit substrate back into the photoresist coating. Standard photoresists are susceptible to surface reflections which degrade the fine-line images required for integrated circuit manufacture. This degradation occurs due to reflection of diffused light from the integrated circuit substrate back into the photoresist layer resulting in exposure of the photoresist layer in areas where imaging is not desired.

To prevent reflection of activating radiation into a photoresist coating, it is known to provide antireflective layers (ARC's) between a substrate and a photoresist layer. These antireflective layers typically comprise an adsorbing dye dispersed in a polymer binder though some polymers contain sufficient chromophores whereby a dye is not required. When used, the dye is selected to adsorb and attenuate radiation at that wavelength used to expose the photoresist layer thus reducing the incidence of radiation reflected back into the photoresist layer. During the conventional processing of an integrated circuit substrate coated with the combination of an antireflective layer and a photoresist layer, the photoresist is exposed to activating radiation and developed to form a relief image, i.e., portions of the photoresist layer are removed by development with a liquid developer and portions remain as a mask defining a desired pattern. To alter the underlying substrate, the antireflective layer must be removed to bare the substrate in a desired image. Removal of the antireflective layer may be by dissolution with a liquid that simultaneously dissolves both the photoresist and the antireflective layer or by dry etching such as with an oxygen plasma.

In those processes using solely wet development, the developer used to develop the imaged photoresist layer also dissolves the underlying antireflective layer. However,

simultaneous development of the photoresist coating and the underlying antireflective coating often leads to undercutting of the imaged photoresist coating caused by the developer seeping beneath those portions of the photoresist coating which are insoluble in developer. The seepage causes dissolution of the antireflective coating beneath the photoresist layer and partial lift-off of the photoresist coating at the relief image margins resulting in a loss of fine line image resolution.

To avoid undercutting of the antireflective coating during development of the photoresist coating, dry etching of the antireflective coating such as with an oxygen plasma has been used. In this process, the antireflective coating used is one that is insoluble in developer for the imaged photoresist. Therefore, contact of the imaged photoresist coating with the developer does not dissolve the underlying antireflective coating. Following development, the structure formed consists of the substrate coated with the antireflective layer overcoated with a photoresist in a desired relief image pattern which functions as a mask over the antireflective layer. Following development of the photoresist coating, the antireflective coating bared by removal of the photoresist is removed by dry etching the entire surface of the coated wafer, typically with an oxygen plasma to ash the antireflective layer and thereby form the desired relief image over the integrated circuit substrate. Details for plasma etching can be found in Elliott, *Integrated Circuit Fabrication Technology*, McGraw Hill Book Company, 1982, pp 259 to 308, incorporated herein by reference.

The process utilizing dry etching also suffers several disadvantages. One disadvantage is that the step of dry etching is an additional step requiring special equipment that adds to the overall processing sequence time and cost for the fabrication of the integrated circuit. Moreover, plasma etching is a blanket etching step whereby the photoresist mask and the antireflective coating are both exposed to the plasma. This often leads to degradation of the overlying photoresist coating resulting in an uneven and partially removed photoresist coating. Nonuniformity of the coating caused by a dry etch step increases variations in the delineated microcircuitry sizing following the etch. Reduction in the thickness of the mask comprising the photoresist and underlying delineated antireflective layer decreases the thickness of the coating available for masking the substrate.

In addition to difficulties encountered with removal of the antireflective coating, other problems are often encountered when an antireflective coating is used in combination with a photoresist coating. One such problem is that of carefully selecting an antireflective coating that is compatible with the photoresist used. The antireflective coating should be inert with respect to the photoresist coating while firmly bonding to the coating. It is desirable that the antireflective coating be chemically inert to avoid photoresist contamination caused by migration of chemical species from the antireflective coating into the photoresist coating that could alter or degrade the response of the photoresist to activating radiation and development. At the same time, it is necessary that the antireflective coating firmly bond to the photoresist coating to avoid lift-off of the photoresist coating during processing of the underlying substrate.

It is therefore an object of this invention to provide a process for preventing reflection of activating radiation by use of an antireflective coating where removal of the antireflective coating is by a process other than by dry etching or simultaneous wet development of both a photoresist layer and the antireflective layer.

A further object of this invention is to decrease reflection of light into a photoresist layer by use of a process whereby

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the thickness of an antireflective layer may be increased to make the same more opaque.

A still further object is to reduce the process cycle time for the manufacture of integrated circuits using antireflective coatings.

An additional object of this invention is to increase adhesion between an antireflective coating and a photoresist mask.

A primary object of this invention is to preserve the fine lines desired in an exposed and developed photoresist mask and in an image transferred to an underlying substrate.

Other objects and advantages will become apparent from the following more complete description and claims.

SUMMARY OF THE INVENTION

Broadly, the invention contemplates a process for reducing reflection from a substrate such as an integrated circuit substrate during imaging of a photoresist layer coated over said substrate using an antireflective coating. The process comprises the steps of providing a developer-insoluble antireflective coating over a substrate, providing a photoresist layer over said antireflective layer, imaging the photoresist layer by exposure and development of the same with a developer that does not dissolve the antireflective layer to form a relief image over the antireflective layer, altering the solubility properties of the antireflective layer in areas bared by removal of the photoresist using a combined step of exposure and heating, and removing the antireflective layer by contact with a solvent for the antireflective layer which does not appreciably attack or solvate the overlying hardened photoresist layer.

The above-described process is characterized by the steps of altering the solubility properties of the bared portions of the antireflective layer while heating and exposing the same without altering the dissolution properties of the antireflective coating masked by the photoresist coating. The step of heating accelerates the step of altering the dissolution properties of the antireflective coating by exposure to light, cures or hardens the photoresist mask overlying the antireflective coating, and enhances the bond between the antireflective coating and the photoresist mask. The process enables development of the antireflective layer without undercutting beneath the photoresist layer and without removing a portion of the overlying photoresist layer during the step of development while avoiding a dry etching step to remove the antireflective layer.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

In the practice of the process of this invention, a substrate such as a silicon wafer is coated with an antireflective coating such as by spin coating. If required, the coated wafer may then be baked at elevated temperature to cure the coating. If heated, the coated wafer is allowed to cool and is coated with a photoresist composition such as by spin coating. The photoresist composition is then dried, exposed to activating radiation to form an acid catalyst in an image pattern, heating the photoresist to convert the exposed areas using a thermally activated catalytic reaction, and developed with a developer that does not dissolve the underlying antireflective coating. Following development, the unmasked or bared area of the antireflective coating is removed by altering its solubility properties using a heating step and dissolving the same in a suitable solvent.

In a preferred embodiment of the invention, to be described in greater detail below, solubility of the antire-

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flective layer is altered by exposing the coating to activating radiation while heating the same to an elevated temperature. The temperature selected is one that accelerates chain scission of a developer-insoluble polymer comprising the antireflective layer to render the same developer soluble while simultaneously hardening or curing the overlying photoresist mask and enhancing the bond between the mask and the underlying antireflective layer. Heating is for a period of time sufficient to convert the developer-insoluble antireflective coating to a developer-soluble species while hardening the photoresist layer. Though the temperature is dependent upon the materials comprising the antireflective layer and the photoresist, in the preferred embodiment of the invention, the temperature is preferably in excess of 100° C. though lower temperatures may be used as will be described below. After the conversion of the antireflective layer, the hardening of the photoresist mask and the bonding of the photoresist mask to the antireflective layer, the antireflective coating is removed by contact with a developer such as an aqueous base solution. This step of development removes the antireflective coating in the non-masked areas thus exposing the integrated circuit substrate in a desired fine-line image pattern. Following this procedure, the substrate may be left unchanged or modified in a conventional manner.

The photoresist used in the above process is not critical though it should be selected to avoid intermixing or chem absorption with the antireflective layer as would be obvious to those skilled in the art and provided that it is capable of undergoing hardening or curing at elevated temperatures.

Suitable photoresist compositions are well known in the art and described in numerous publications including DeForest, Photoresist Materials and Processes, McGraw-Hill Book Company, New York, 1975. Photoresists comprise coatings produced from solution or applied as a dry film which, when exposed to light of the proper wavelength, are chemically altered in their solubility to certain solvents (developers). Two types are known. The negative-acting resist is initially a mixture which is soluble in its developer, but following exposure to activating radiation and in some cases, heat treatment, becomes insoluble in developer thereby defining an image. Positive-acting resists work in the opposite fashion, light exposure making the resist soluble in developer immediately following exposure, or in some cases following exposure and heat treatment.

The positive-working resists may comprise a light-sensitive compound in a film-forming polymer binder. The light-sensitive compounds most frequently used are esters formed from o-quinone diazide sulfonic acids. These esters are well known in the art and are described by DeForest, supra, pages 47–55, incorporated herein by reference. These light-sensitive compounds, and the methods used to make the same, are all well documented in prior patents including German Pat. No. 865,140 granted Feb. 2, 1953 and U.S. Pat. Nos. 2,767,092; 3,046,110; 3,046,112; 3,046,119; 3,046,121; 3,046,122; and 3,106,465, all incorporated herein by reference.

A class of negative resists comprising a negative-acting sensitizer in a polymer binder is described by Iwayanagi et al., IEEE Transactions on Electron Devices, Vol. ED-28, No. 11, November, 1981, incorporated herein by reference. The resists of this reference comprise an aromatic azide in a phenolic binder. It is believed that these resists were first disclosed and claimed in U.S. Pat. No. 3,869,292, also incorporated herein by reference. Additional aromatic azide sensitizers are disclosed by DeForest, supra, and U.S. Pat. Nos. 2,940,853 and 2,852,379, incorporated herein by reference.

The resin binders most frequently used with the o-quinone diazides in commercial practice are the alkali-soluble phenol formaldehyde resins known as the novolak resins. Photoresists using such polymers are illustrated in U.K. Pat. No. 1,110,017, incorporated herein by reference. These materials are the product of reaction of a phenol with formaldehyde under conditions whereby a thermoplastic polymer is formed with a glass transition temperature of about 100° C.

Most of the above photoresists are imaged by exposure to I-Line or G-Line irradiation. Recently interest has increased in photoresists that can be photoimaged with deep ultraviolet radiation. Such photoresists enable formation of smaller features than possible at longer wavelength exposure. As is recognized by those in the art, "deep U.V. radiation" refers to exposure radiation having a wavelength in the range of about 350 nm or less, and more typically is in the range of about 300 nm or less. A photoresist formulation suitable for deep U.V. exposure is disclosed in U.S. Pat. No. 5,344,742, incorporated herein by reference. Photoresists capable of imaging by exposure to deep U.V. radiation and processes using such photoresists are preferred for purposes of this invention.

Antireflective coating compositions and their uses are also known in the art and are described in numerous articles such as in the *IEEE Transactions on Electron Devices*, Edition 28, No. 11 of Nov. 1981, pages 1405 through 1410, entitled "Line Width Control and Projection Lithography Using a Multi-Layer Resist Process" by O'Toole et al. and in "Reduction of the Standing Wave Effect in Positive Photoresist," Brewer et al. in *Journal of Applied Photographic Engineering*, Vol. 7, No. 6, Dec. 1981, pages 184 through 186, and "Control of One-Micron Lines in Integrated Circuits," Carlson et at., *Kodak*, '80 Interface, Oct. 1980, pages 109 through 113, and in U.S. Pat. Nos. 4,370,405; 4,668,166; 4,719,166; 4,828,960; 4,910,122; and 5,234,990, each incorporated herein by reference.

Typical antireflective coatings comprise an adsorbing dye dispersed in a suitable polymer binder in an amount sufficient to attenuate the reflection of activating radiation into a photoresist coating. In some formulations, the resin binder contains sufficient chromophores to enable adsorption of activating radiation without the use of a separate dye. Typically, when a dye is added, it is used in an amount of about 0.1 to 10 grams per liter of coating composition and more preferably, in an amount of from 1 to 5 grams per liter of coating composition. In selection of the dye, care should be exercised to assure that the dye is compatible with the photoresist used and is thermally stable at processing temperatures used. Further, the dye shall be non-volatile at the temperature used and must adsorb reflective radiation at the radiation wavelength used to expose the photoresist. Among the dyes which may be used are 2-(P-(dimethylamino) phenylazo) benzoic acid (Methyl red), 4-(phenylazo) resorcinol (Sudan orange) and di-n-butyl-(5-di-n-butylamino-2,4-pentadienylidene)-ammonium perchlorate. Polymers that may be used with or without dyes include aromatic urea sulfone and aromatic sulfone polymers.

The antireflective coating selected is one capable of having its dissolution properties altered following development of the overlying photoresist coating. A lesser preferred method of altering dissolution properties is to add a photoactive compound to the antireflective coating responsive to activating radiation at a wavelength differing from the radiation used to image the photoresist coating. For example, if the photoresist is one imaged by exposure to deep ultraviolet radiation, the photoactive compound used may be one activated by I-Line or G-Line irradiation. In this

way, exposure of the photoresist would not alter the dissolution properties of the underlying antireflective layer. Following exposure and development of the photoresist, the antireflective layer bared by removal of the photoresist coating would be imaged using radiation at that wavelength capable of altering the dissolution properties of said layer.

In an alternative embodiment of the invention, an antireflective coating photoresist combination can be used where the antireflective coating undergoes chain scission at a wavelength where the photoresist is opaque. For example, an I-Line or G-Line activated photoresist can be used with an antireflective coating which undergoes chain scission at deep ultraviolet exposure. In this embodiment of the invention, the photoresist would be exposed to I-Line or G-Line irradiation, for example, and developed baring the underlying antireflective coating. The antireflective coating would then be exposed to irradiation with heating to cause chain scission such as deep ultraviolet irradiation, but which would not enhance the dissolution of the overlying photoresist. Thereafter, the antireflective coating could be altered by contact with a suitable developer.

In a preferred embodiment of the invention, the antireflective coating is one capable of undergoing chain scission by exposure to activating radiation to alter its solubility properties. Typically, chain scission is accelerated at elevated temperatures. Consequently, exposure of the antireflective coating takes place at an elevated temperature, especially those elevated temperatures that simultaneously harden or cure an overlying photoresist mask and enhance the bond between the mask and the antireflective coating. Further, it is desired that the antireflective coating is one that undergoes chain scission by exposure to radiation at a wavelength that is the same wavelength used to cross-link the photoresist coating thus avoiding the need for two imaging tools. The preferred embodiment of the invention described above is possible with a combination of either a positive-acting thermally-activated chemically-amplified photoresist or that acid hardened deep ultraviolet photoresist that is the subject of U.S. Pat. No. 5,344,742 and those preferred polysulfone antireflective coating compositions disclosed in U.S. Pat. No. 5,234,990, especially that polysulfone that is a copolymer of 4,4'-isopropylidenediphenol and 4-chlorophenylsulfone. These materials are preferred because it has been discovered that the polysulfone antireflective coatings are converted from base insoluble to base soluble coatings by exposure to radiation within a broad band of from about 250 to 450 nm while heating to a temperature of 20° C. or higher. The chemically amplified photoresists and the acid-hardened photoresists do not appreciably solubilize at temperatures below 50° C., solubilize at temperatures between about 50° C. and 100° C., and cure or harden at temperatures above 100° C. Consequently, antireflective coatings formed from these polysulfones coated with either an imaged positive-acting thermally-activated chemically-amplified photoresist or an acid-hardened deep ultraviolet photoresist can be exposed to radiation within the range of 250 to 450 nm while heating to a temperature of from about 20° C. to 50° C. or at a temperature of in excess of 100° C., typically up to about 200° C. or that temperature that causes thermal degradation of either the antireflective coating or the photoresist mask. Accordingly, when the polysulfone antireflective coating is used in combination with the acid-hardened deep ultraviolet photoresist coating, the photoresist may be exposed and developed with a developer that does not solubilize the antireflective coating formed from the polysulfone to form a mask over the antireflective coating, the bared antireflective

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coating is exposed such as by blanket exposure to irradiation within the range of from 250 to 450 nm while heating, and then the bared antireflective coating is removed by contact with a solution of an aqueous base such as a conventional photoresist developer. The exposure is to a wavelength that converts the base insoluble antireflective coating to a base soluble material. Exposure of the antireflective coating to the shorter wavelengths (below 380 nm) enhances the chain scission of the antireflective coating but also tends to deblock the blocking groups of the photoresist tending to solubilize the same thereby requiring higher temperatures for cure of the photoresist layer to overcome the effect of deblocking on solubility of the photoresist. Exposure to the higher wavelengths (380 nm and above) does not cause deblocking within the photoresist mask and lower temperatures may be used to cure the photoresist coating. The developer may be an aqueous alkaline 0.1N to 0.5N solution of tetramethyl ammonium hydroxide.

The above-referenced U.S. Pat. No. 5,234,990 discloses that exposure of a composite of the polysulfone and the photoresist to activating radiation permits development of both during the step of development of the photoresist. However, to accomplish this, the exposure dose must be excessive or the antireflective layer must be thin in order to cause adequate scission of the polysulfone layer whereby it becomes base soluble. An excessive exposure dose over-exposes the photoresist resulting in a loss of image quality. A thin antireflective layer inadequately attenuates reflected light from the substrate. Consequently, the invention described herein differs from the invention of said patent by use of an exposure dose sufficient to expose the photoresist but insufficient to significantly solubilize the antireflective layer.

As a further advantage to the invention, it has been found that the heating step during exposure of the antireflective layer also improves the bond between the antireflective layer and the photoresist mask. This is an advantage to the process, both during the step of development of the antireflective layer and during the subsequent steps of altering the underlying wafer.

The antireflective coating and photoresist layer may be applied sequentially to a substrate in a conventional manner. Each may be spin coated or roller coated as a liquid coating composition onto a suitable substrate. Following the step of coating the liquid coating composition onto the substrate, the coating is dried by heating the same to a suitable drying temperature such as about 100° C. for a time sufficient to remove substantially all solvent and provide a non-tacky coating layer. Typically, the average thickness of the anti-reflective coating may range between about 750 and 1,300 Angstroms and the photoresist coating may vary between 4,000 and 12,000 Angstroms dependent upon the masking requirements of the photoresist.

The invention will be better understood by reference to the following example.

EXAMPLE

A 200 mm clean silicon wafer was primed with hexam-ethyldisilizane. The prepared wafer was coated by spin coating with Brewer CD9 antireflective coating and cured at 224° C. for 60 seconds to form a coating having a thickness of 1100 Angstroms. The Brewer antireflective coating comprised a polysulfone in a coating solvent. Thereafter, the dried antireflective coating was coated with a deep ultraviolet photoresist obtained from Shipley Company LLC and identified as APEX-E deep ultraviolet photoresist. The wet coating was dried and post-exposure baked at 100° C. for 60 seconds to provide a coating having a thickness of about 10,000 Angstroms. The dried photoresist coating was then exposed using a GCA XLS 0.53 numerical aperture through a 248 nm deep ultraviolet stepper. The composite coated with the exposed photoresist coating was then hot-plate baked at 90° C. for 60 seconds. The exposed photoresist coating was spray and double-puddle developed using 0.21 normal tetramethyl ammonium hydroxide solution containing proprietary surfactants for 60 seconds at 22° C. to yield a relief image in the photoresist coating with the underlying antireflective layer bared in the recesses. The developer used was obtained from Shipley Company LLC and sold under the trade designation MF-321 Developer. Following development, the coated wafer was subjected to a ultraviolet irradiation and thermal cured using a Fusion Systems H-modified lamp. Temperature was adjusted to 110° C. while the lamp was turned on at low power for 10 seconds while maintaining the temperature at 110° C. The lamp was then turned to high power, and the temperature ramped upward from 110° C. to 160° C. using a 35-second linear ramp rate. Following this step of exposure and heating, the exposed antireflective coating was removed by spray and double-puddle development using the Shipley Company LLC MF-321 Developer for 60 seconds at 22° C. to provide a relief image in both the photoresist coating and the antireflective coating. The lines within the relief image of the photoresist and antireflective coating were 0.35 microns and smaller. Following transfer of the image to the underlying substrate, the composite of the photoresist and antireflective coating is removed by dry etching with oxygen or by solvent dissolution.

We claim:

1. A process for reducing reflection from a substrate during imaging of a photoresist layer, said process comprising the steps of forming an antireflective, radiation-adsorbing coating over a substrate; applying a radiation-sensitive photoresist layer over said antireflective coating, said antireflective coating being capable of adsorbing activating radiation for said photoresist layer thus decreasing reflection of the same back into the photoresist layer; exposing said photoresist layer to activating radiation in an image pattern to form a latent image therein without formation of a developable latent image in the antireflective coating, developing said photoresist layer with a developer that is incapable of dissolving said antireflective coating to form a relief image in said photoresist layer, altering the dissolution properties of the antireflective coating; and dissolving said antireflective coating in a solvent therefor without appreciably dissolving the photoresist layer to bare the underlying substrate in an image pattern.

2. The process of claim 1 where the composite of the substrate, antireflective coating and photoresist layer are heated to elevated temperature during the step of altering the dissolution properties of the antireflective coating.

3. The process of claim 2 where the photoresist layer is one activated by exposure to deep ultraviolet irradiation and the antireflective coating is one that adsorbs deep ultraviolet irradiation.

4. The process of claim 2 where the photoresist layer is a positive-working photoresist.

5. The process of claim 2 where the photoresist layer is a negative-acting photoresist.

6. The process of claim 2 where the exposed photoresist layer containing a latent image is soluble in an aqueous base solution and the antireflective coating is insoluble in said aqueous base solution.

7. The process of claim 2 where the antireflective coating is altered to render the same soluble in an aqueous base solution.

8. The process of claim 7 where the antireflective coating is altered in its dissolution properties by heating said coating while exposing the same to radiation capable of causing chain scission of said coating.

9. The process of claim 8 where the antireflective coating and the photoresist layer are heated to a temperature capable of accelerating the rate of alteration of said antireflective coating and curing the photoresist layer to render said layer insoluble in developer for the antireflective coating.

10. The process of claim 9 where the temperature varies between 20° C. and that temperature that would insolubilize the photoresist layer in developer for the antireflective coating.

11. The process of claim 9 where the temperature varies between 100° C. and that temperature that would degrade the photoresist layer.

12. The process of claim 11 where the maximum temperature is 200° C.

13. The process of claim 8 where the antireflective coating is exposed to a wavelength of below 380 nm.

14. The process of claim 8 where the antireflective coating is exposed to a wavelength of from 190 nm to 230 nm.

15. A process for reducing reflection from an integrated circuit substrate during imaging of a photoresist layer, said process comprising the steps of forming a polysulfone coating capable of adsorbing deep ultraviolet radiation over an integrated circuit substrate; applying a deep ultraviolet radiation-sensitive photoresist layer over said polysulfone coating; exposing said photoresist layer to deep ultraviolet radiation in an image pattern to form a latent image therein without formation of a developable latent image in the polysulfone layer; developing said photoresist layer with an aqueous alkaline developer that is incapable of dissolving said polysulfone coating to form a relief image in said photoresist layer; altering the dissolution properties of the polysulfone coating and the photoresist layer by exposing the same to deep ultraviolet irradiation while heating the same to render the polysulfone coating base soluble and cure the photoresist layer to thereby decrease its base solubility; and dissolving said polysulfone coating in an aqueous alkaline developer solution to bare the underlying substrate in an image pattern.

16. The process of claim 15 where the photoresist layer is of a negative-working photoresist.

17. The process of claim 15 where the photoresist layer is of a positive-working photoresist.

18. The process of claim 17 where the positive-working photoresist is a chemically amplified or acid-hardened photoresist.

19. The process of claim 17 where the antireflective coating and photoresist layer are heated to a temperature of from 20° C. to that temperature that would degrade the photoresist layer without solubilizing the photoresist layer in developer for the antireflective coating.

20. The process of claim 19 where the temperature varies between 20° C. and 50° C. or from 100° C. to 200° C.

21. The process of claim 15 where the antireflective coating is exposed to a wavelength of below 380 nm.

22. The process of claim 15 where the antireflective coating is exposed to a wavelength of from 190 nm to 230 nm.

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United States Patent [19]

Gronbeck et al.

[54] **PROCESS FOR REMOVING HEAVY METAL IONS BY ION EXCHANGE**

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[52] U.S. Cl. **210/686**; 210/688

[58] Field of Search 210/686, 688, 210/912, 913

[56] **References Cited**

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5,525,315	6/1996	Burke	210/688
5,571,657	11/1996	Szmanda et al.	210/688

FOREIGN PATENT DOCUMENTS

93/12152   6/1993   WIPO .

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[57] **ABSTRACT**

The invention is for a process of removing dissolved heavy metal cation contaminants from an organic solution. The process of the invention involves providing a mixture of a chelating ion exchange resin modified by removal of sodium ions therefrom and an anion exchange resin and contacting said organic solution with said exchange resins for a time sufficient to remove ionic metal impurities and acids. The invention is useful for removal of ionic contaminants from organic solutions requiring high purity.

20 Claims, No Drawings

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PROCESS FOR REMOVING HEAVY METAL IONS BY ION EXCHANGE

BACKGROUND OF THE INVENTION

1. Introduction

This invention relates to removal of dissolved contaminants from organic solutions. More particularly, this invention relates to removal of dissolved metallic and acidic contaminants from organic solutions used in integrated circuit manufacture.

2. Description of the Prior Art

Ultra pure liquids free of particulate, ionic and organic contamination are required for many industrial purposes such as for the manufacture of pharmaceuticals and for the fabrication of integrated circuits. For example, in the manufacture of high resolution integrated circuits, it is known that many processing liquids come into contact with a bare wafer or resist coated surface. These include photoresists and treatment chemicals such as organic liquids and aqueous solutions which contain acids, bases, oxidants, and other proprietary ingredients. At least 15 to 50 liquids of various compositions are used to clean wafers, prime surfaces, deposit resists or other polymers, develop, rinse, etch or strip resist. It is known that these solutions may be a source of contamination of the integrated circuit wafer which may interfere with its performance. Thus, the reduction or removal of insoluble and soluble contaminants from processing fluids used for the production of integrated circuits before or during use is basic to prevent damage to the integrated circuit.

Photoresist coating compositions are used extensively in integrated circuit manufacture. Such compositions typically comprise a light-sensitive component and a polymer binder dissolved in a solvent. Typical photoresist compositions are disclosed in U.S. Pat. Nos. 5,178,986; 5,212,046; 5,216,111; and 5,238,776, each incorporated herein by reference for disclosure of photoresist compositions, processing of resist coatings and use.

It is known that photoresist coating compositions contain particulate and ionic contaminants. For example, it is known that solid gels or irksolubles form in photoresists due to reactions of the photoactive component of the resist. In addition, soluble impurities such as moisture, silicone oils, plasticizers, acid and bases and metal ions may be present from the manufacture of the resist components and from packaging containers or dispensing tanks for the resists. In addition to contaminants, bubbles from point-of-use filtration or the shaking of a resist bottle prior to dispensing can lead to defects in a resist coating. In Class 100 clean rooms, airborne particulate counts amount to 3 particles per liter. By comparison, liquids contain about 100.000 particles per liter. A particle count of 100,000 per liter seems high, but if translated into a solid of 0.6 µM in size, this is equivalent to 10 parts per million parts of solution (ppm). A level of 10 ppm amounts to the deposition of 10 mg per liter. Since liquids are heavily contaminated compared to clean room air, effective contaminant removal is essential to the manufacture of devices requiring ultra pure materials.

Ultrafiltration of resist liquids has progressed and manufacturers of resist now supply resist materials filtered through 0.04 µM diameter absolute filters. However, methods for removal of particulates from treatment solutions are not effective for removal of dissolved contaminants from solution such as organic impurities and ionic species. These contaminants can be at least as damaging to integrated circuit performance as particulate contamination.

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Efforts to remove dissolved cationic and anionic contaminants from treatment solutions used to manufacture integrated circuits are known in the art. For example, one such method, disclosed in International Publication No. WO 93/12152 and incorporated herein by reference, is directed to removing metal ions such as sodium and iron from novolak resins during manufacture. The process comprises cation exchange treatment whereby a cation exchange resin is first washed with a mineral acid solution to reduce the level of total sodium and iron ions within the exchange resin to preferably less than 100 ppb, passing a formaldehyde reactant through the so treated cation exchange resin to decrease the sodium and iron ion content to less than 40 ppb, passing a phenolic compound through the cation exchange resin to decrease its sodium and iron ion content to less than 30 ppb, and then condensing the so treated phenolic compound with formaldehyde in the presence of an acid catalyst to form the resin.

A method for removal of dissolved ionic metals and non-metals from a photoresist is disclosed in published Japanese Patent Application No. 1228560 published Sep. 12, 1989, incorporated herein by reference. In accordance with the procedures of this patent, a photosensitive resin is passed through a mixed bed of cation exchange resin and an anion exchange resin to simultaneously remove cation and anionic species from the photoresist solution.

In U.S. Pat. No. 5,571,657 incorporated herein by reference, an improved process is disclosed for removing metallic cations from organic solutions using modified cation exchange resins. In accordance with the process of the invention disclosed therein, the cation exchange resin is modified by replacement of the acid protons on the cation exchange groups with essentially neutral groups such as ammonium or amine groups. Thereafter, an organic solution containing acid labile components may be treated with the modified cation exchange resin to remove metal ions without the formation of undesired by-products caused by attack of acid protons on acid labile groups.

The process described in the above-identified patent is suitable for the removal of dissolved cations from solutions containing an acid labile solution. The process is especially useful for removing mobile metal ions such as sodium and potassium from such solutions. However, the process is less effective for removing heavier metal ions such as iron and chromium from solution.

In U.S. Pat. No. 5,525,315, incorporated herein by reference, a process is provided whereby organic solutions are treated to remove large concentrations of dissolved heavy metal ions using chelating exchange resins. The process comprises providing a cation exchange resin having chelating groups on the resin, treating the resin with an acid to replace sodium ions typically associated with such resins with a hydrogen proton, and contacting the organic solution with said resin to remove dissolved metallic contaminants.

Treatment of the chelating cation exchange resin with an acid results in replacement of sodium ions from the exchange groups thereby preventing contamination of the solution to be treated with the more mobile sodium ions. The removal of sodium ions from the resin is especially important for the purification of organic solutions containing dissolved components used in the formulation of compositions to be used in integrated circuit manufacture.

The process of the above referenced patent effectively removes heavy metal ions from solution, but the step of replacement of sodium ions with acid results in acid groups on the chelating exchange resin. When the organic solution

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is passed through the chelating exchange resin. acids are introduced into the solution which are unacceptable for photoresist use. This is especially true for photoresists that utilize acid hardening chemistry such as photoresists containing photoacid generators or acid labile groups to obtain differential solubility. Such photoresists are illustrated in U.S. Pat. Nos. 5,182,232 and 5,541,263 and published European applications Nos. 0 164 248 and 0 232 972, each incorporated herein by reference for their disclosure of acid hardening photoresists.

SUMMARY OF THE INVENTION

The process of the present invention is an improvement over the process of U.S. Pat. No. 5,525,315 in that means are used to remove both the heavy metal ions and acid introduced into the resin by the chelating exchange resin. In accordance with the invention, a treated anion exchange resin is homogeneously mixed with the chelating exchange resin to remove heavy metal ions simultaneously with removal of liberated acids.

The process of the invention comprises treatment of a chelating exchange resin with a strong acid solution and washing the so treated resin with water to neutral pH, water washing of an anion exchange resin, admixture of the two to form a uniform mixture where the molar concentration of the base groups on the anion exchange resin do not exceed the moles of acid generated during treatment of an organic solution with the exchange resin mixture, dehydration of the mixed resins and passage of the organic solution through the bed of the mixed ion exchange resin. Preferably, the ratio of the chelating exchange resin to the anion exchange resin is at least 1:2.

For reasons not fully understood, it has been found that use of the two exchange resins sequentially removes metal ion impurities, but not acids. Use of a homogeneously mixed bed unexpectedly removes both.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The process of the subject invention is applicable to many organic solutions containing dissolved contaminants but is especially useful for treating solutions used in integrated circuit manufacture such as antireflective coating solutions and photoresist solutions, especially solutions containing acid labile components and dissolved metal contaminants in ionic form, especially heavy metal contaminants. Accordingly, the description that follows primarily exemplifies purification procedures for photoresist components and antireflective coatings, especially polymers used to formulate such compositions, but the invention should not be construed as limited to this embodiment.

Photoresists are well known and described in numerous publications including DeForest, *Photoresist Materials and Processes*, McGraw-Hill book Company, New York, Chapter 2, 1975 and Moreau, *Semiconductor Lithography, Principles, Practices and Materials*, Plenum Press, New York, Chapters 2 and 4, 1988, each incorporated herein by reference.

Suitable positive-working photoresists typically contain two components—a light-sensitive compound and a film-forming polymeric binder where the light-sensitive component undergoes photochemical alteration upon exposure. Single component systems are known and typically comprise a polymer that undergoes chain scission upon exposure. The light-sensitive compounds most frequently used in two-component resist systems are esters formed from an

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o-quinone diazide sulfonic acid, especially sulfonic acid esters of naphthoquinone diazide. These esters are well known and described by DeForest, supra, pages 47–55 and by Moreau, supra, pages 34–52. The light-sensitive compounds and the methods used to make the same are all documented in prior patents including U.S. Pat. Nos. 3,046,110; 3,046,112; 3,046,119; 3,046,121; 3,106,465; 4,596,763; and 4,588,670, all incorporated herein by reference.

The polymer binders most frequently used for positive-working photoresists in conjunction with o-quinone diazides are the alkali soluble phenol formaldehyde resins known as the novolak resins. Photoresists using such polymers are illustrated in U.S. Pat. Nos. 4,377,631 and 4,404,272 incorporated herein by reference. Another class of binders used with o-quinone diazides are homopolymers and copolymers of vinyl phenol. Photoresists of this nature are disclosed in U.S. Pat. No. 3,869,292 incorporated herein by reference. The process of the subject invention is especially useful for the purification of the phenolic polymers used to formulate positive-working photoresists.

Negative-working resists and the components thereof may also be treated in accordance with the invention and are well know in the art. Such photoresists typically undergo random crosslinking upon exposure to activating radiation thereby forming areas of differential solubility. Such resists often comprise a polymer and a photoinitiator. One class of negative-working resists comprises, for example, polyvinyl cinnamates as disclosed by R. F. Kelly, Proc. Second Kodak Semin. Microminiaturization, Kodak Publication Property-89, 1966, Property. 31. Other negative-acting resists include polyvinyl-cinnamates as disclosed in U.S. Pat. No. 2,716,102; azide cyclized rubber as disclosed in U.S. Pat. No. 2,940,853; polymethylmethacrylate/tetraacrylate as disclosed in U.S. Pat. No. 3,149,975; polyimide-methyl methacrylate as disclosed in U.S. Pat. No. 4,180,404; and polyvinyl phenol azide as disclosed in U.S. Pat. No. 4,148,655. Each of the aforesaid references is incorporated herein by reference for the teaching of negative photoresist compositions and the use of the same.

Another class of photoresists suitable for treatment in accordance with the process of the invention are those positive and negative acid-hardening resists disclosed in EPO application Ser. No. 0 232 972 in the name of Feely et al, incorporated herein by reference. These photoresists comprise an acid-hardening resin and a halogenated, organic, photoacid generating compound. Additional acid hardening resists are exemplified in the above referenced U.S. Pat. Nos. 5,182,232 and 5,541,263 and published European application Nos. 0 164 248. These photoresists are characterized by use of acid labile components. Photoresists capable of imaging by exposure to deep U.V. radiation and processes using such photoresists are preferred for purposes of this invention.

Antireflective coating compositions and their uses are also known in the art and are described in numerous articles such as in the *IEEE Transactions on Electron Devices*, Edition 28, No. 11 of November 1981, pp. 1405–1410, entitled "Line Width Control and Projection Lithography Using a Multi-Layer Resist Process" by O'Toole et al.; in "Reduction of the Standing Wave Effect in Positive Photoresist," Brewer et al, in the *Journal of Applied Photographic Engineering*, Vol. 7, No. 6, December 1981, pp. 184–186; in "Control of One-Micron Lines in Integrated Circuits," Carlson et al. *Kodak*, 80 Interface, October 1980, pp 109–113; and in U.S. Pat. Nos. 4,370,403; 4,668,166; 4,719,166; 4,828,960; 4,910,122; and 5,234,990, each incorporated herein by reference.

Typical antireflective coatings comprise an adsorbing dye dispersed in a suitable polymer binder in an amount suffi-

cient to attenuate the reflection of activating radiation into a photoresist coating. In some formulations, the resin binder contains sufficient chromophores to enable adsorption of activating radiation without the use of a separate dye. Typically, when a dye is added, it is used in an amount of about 0.1 to 10 grams per liter of coating composition and more preferably, in an amount of from 1 to 3 grams per liter of coating composition. In selection of the dye, care should be exercised to assure that the dye is compatible with the photoresist used and is thermally stable at processing temperatures used. Further, the dye should be non-volatile at the temperature used and must adsorb reflective radiation at the radiation wavelength used to expose the photoresist. Among the dyes which may be used are 2-(P-(dimethylamino) phenylazo) benzoic acid (Methyl red), 4-(phenylazo) resorcinol (Sudan orange) and di-n-butyl-(5-di-n-butylamino-2,4-pentadienylidene)-ammonium perchlorate. Polymers that may be used with or without dyes include aromatic urea sulfone and aromatic sulfone polymers.

The antireflective coating used may be one capable of having its dissolution properties altered following development of an overlying photoresist coating. This may be accomplished by adding a photoactive compound to the antireflective coating responsive to activating radiation at a wavelength differing from the radiation used to image the photoresist coating. For example, if the photoresist is one imaged by exposure to deep ultraviolet radiation, the photoactive compound used may be one activated by I-Line or G-Line irradiation. In this way, exposure of the photoresist would not alter the dissolution properties of the underlying antireflective layer. Following exposure and development of a photoresist coating, the antireflective layer bared by removal of the photoresist coating would be imaged using radiation at that wavelength capable of altering the dissolution properties of said layer.

Regardless of the method used to process the antireflective layer, it may contain any of a dye, polymer, solvents and light sensitive component. Any or all of the same are a source of contaminants and potentially acid labile. Consequently, contaminants must be removed without causing damage to the components of the coating solution.

Substantially all components of a photoresist composition or an antireflective coating composition are a potential source of dissolved metallic contaminants that can deleteriously effect performance of an integrated circuit. Typical dissolved metal contaminants include sodium, potassium, iron, copper, chromium, nickel, molybdenum, and zinc. While it is known to treat photoresist solutions and solutions of photoresist components with exchange resins to remove dissolved metals, it is also know that conventional ion exchange processes for removal of such contaminants are not suitable for reduction in the concentration of the metallic contaminants to the extent necessary for the manufacture of integrated circuits—i.e., to amounts less than 100 parts per billion parts of solution (ppb) and preferably to levels of less than 25 ppb.

The process of the invention utilizes a mixed bed of a chelating cation exchange resin and an anion exchange resin. The chelating cation exchange resin is one capable of chelating with heavy metal ions. For use in accordance with the invention, the chelating exchange resin is modified to replace sodium or other alkali metal on the resin with a hydrogen proton. The use of such a material for treatment of an organic solution removes heavy metal ions. It is less effective for removal of the more mobile metal ions such as potassium and sodium ions and it may be desirable to treat the solutions containing both mobile metal ions and heavy

metal ions with the chelating ion exchange resin of the invention and another ion exchange resin capable of removing mobile metal ions such as the modified cation exchange resins disclosed in U.S. Pat. No. 5,571,657 incorporated herein by reference.

Chelating cation exchange resins are known and described in numerous publications. for example, suitable exchange materials are disclosed by Samuelson, *Ion Exchange Separation Analytical Chemistry,* John Wiley and Sons, New York, 1963, pp. 33, 69, 87, and 88, and in the Meyers, *Encyclopedia of physical Science and Technology,* Second Edition, Harcourt Brace Jovanovich, San Diego, 1992, Volume 3, pp. 363 to 367, each incorporated herein by reference. Typical chelating exchange resins are polyamines on polystyrene, polyacrylic acid or polyethyleneimine backbones; thiourea on polystyrene backbones; quinoline on polystyrene backbones; dithiocarbamate on a polyethyleneimine backbone; hydroxamic acid on a polyacrylate backbone; hydroxamic acid on a (methy)acrylate-divinyl benzene copolymer, mercapto on polystyrene backbones; and cyclic polyamines on polyaddition and polycondensation resins. Preferred chelating exchange resins for purposes of this invention are styrene-divinylbenzene copolymers having iminodiacetate groups where two carboxyl groups and the tertiary nitrogen give the resin a chelating capability. Such resins are commercially available as Dow Chelex 100 and Dowex A-1, both available from Dow Chemical Company; Diaion CR-10 available from Mitsubishi; Unicellex UR-10 available from Unitica Chemical; Lewatit TP 207 available from Bayer Corporation; and Amberlite IRC-718 from Rohm and Haas Company. The most preferred embodiment of the invention is the treatment of a resin used to form a photoresist with Amberlite IRC-718 acidified with hydrochloric acid.

The chelating cation exchange resins are typically available in sodium salt form. As discussed above, the sodium ion must be removed from the resin prior to its use to prevent sodium from entering the organic solution treated with the resin. This is accomplished by rinsing the resin with a strong acid. Mineral acids are preferred. Hydrochloric acid is most preferred. It is desirable to avoid use of nitric acid because it is capable of causing undesked side reactions such as nitration and oxidation. Sulfuric acid is satisfactory but does not perform as well as hydrochloric acid.

The chelating ion exchange resin is deskably treated to remove sodium ions by rinsing with an aqueous solution of any of the above acids. Hydrochloric acid is preferred in a concentration of at least 6 molar. The solution used to rinse the exchange resin may contain the acid in a concentration of from 1 to 25 percent by weight and more preferably in a concentration of from 18 to 22 percent by weight. Treatment conditions are not critical. Passing a solution of the acid through a bed of the resin is less effective than slurrying the resin with the acid for a prolonged time. Contact time between exchange material with the treatment solution may vary between about 1 and 30 hours and more preferably, from about 1 to 10 hours. In general, the treatment time is sufficient to provide an exchange resin having a pH varying between about 1 and 6 and more preferably between about 1 and 4.

In accordance with the invention, the chelating ion exchange resin is mixed with an anion exchange resin. The two resins are desirably mixed to form a relatively homogenous mixture. Strong anion exchange resins are typically based upon copolymers of styrene and divinyl benzene which have been chloromethylated and then aminated. The aminated resin is then used to form a quaternary ammonium

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functional group. Weak base anion exchange resins are also formed from styrene-divinyl benzene copolymers which are chloromethylated and aminated in a two-step process. Chloromethyl groups are attached to the aromatic rings by reaction of a compound such as chloromethyl ether with the copolymer in the presence of a Friedel-Crafts catalyst such as aluminum chloride. Functionalization is completed by aminating the chloromethylated copolymer with either a primary or secondary amine. Ion exchange resins of the type described are well known in the art and described in numerous publications including Kirk-Othrner, Encyclopedia of Chemical Technology, Volume 14, (Fourth Edition), 1995, pp. 737–783, especially pp. 737–749, incorporated herein by reference for their teaching of typical anion exchange resins.

Suitable anion exchange resins include Amberlite IRA-904 which is a styrene-divinyl benzene resin having quaternary ammonium chloride substitution, Amberlite IRA-958 which is an acrylic-divinyl benzene resin having quaternary ammonium chloride substitution, and Duolite A-191 and Duolite A-192, both of which are styrene-divinyl benzene resins having quaternary ammonium chloride substitution. Other ion exchange resins suitable for purposes of the invention would be obvious from the foregoing. Preferred anion exchange resins are the Amberlites LRA-93, IRA-96, IRA-68, IRA 900 and IRN-78.

The next step in the process of the invention comprises forming a mixture of the chelating exchange resin and anion exchange resin. The amount of the anion exchange resin added to the chelating exchange resin is based upon the moles of base groups on the resin. Sufficient anion exchange resin should be used whereby the number of moles of base does not exceed the moles of acid to be removed from solution. It would be expected that the base should exceed the acid content to effect efficient acid removal. However, in practice, it has been found unexpectedly found that excessive base resin acts as a diluent. Preferably, the molar ratio of base groups to acid groups should vary between 1.2 to 10 and 1 to 1.5 and more preferably, between 1 to 2 and 1 to 4.

Following combination of the two exchange resins, the resin mixture is preferably dehydrated by washing the mixture with an aqueous miscible organic solvent such as ethyl lactate, acetone or a solvent common to the solution to be purified. The procedure can be performed at room or elevated temperature though elevated temperature results in increased exchange efficiency, but with possible concomitant degradation of temperature sensitive materials.

Organic solutions are treated with the modified ion exchange resins by slurrying the same with the resin mixture or by passing the solution through a column of a resin mixture. The rate of passage of the solution through the column can vary between about 2 and 20 bed volumes per hour. Ambient conditions are suitable.

The invention will be better understood by reference to the examples that follow.

EXAMPLE 1

Preparation of chelating exchange resin: A chelating ion exchange (IX) resin identified as Amberlite IRC-718, available from Rohm and Haas Company, was prepared for use by charging one liter of 6M hydrochloric acid solution and 600 gms of the chelating resin to a 2 L reaction vessel equipped with a stopcock on the bottom, a polished glass stirring rod with a polypropylene turbine, and mechanical stirrer. The chelating resin slurry was agitated for 3 hours at a speed sufficient for thorough mixing, but slow enough to prevent damage to the chelating resin beads.

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The chelating resin—HCl slurry was drained into a 5 cm diameter by 30 cm high column and washed continuously with 18Ω deionized water (flow rate of 15–25 mL/min.— approximately 10 bed volumes) until the runoff pH increased to 7.00±0.5. The chelating resin was drained of water, dehydrated with acetone (one bed volume) followed by ethyl lactate (three bed volumes), and stored in ethyl lactate. Dehydration was considered complete when the effluent solvent had a moisture content of less than 0.5%.

EXAMPLE 2

Preparation of anion exchange resin: An anion exchange resin, identified as Amberlite IRA-93, available from Rohm and Haas Company was prepared for use. A 1200 g quantity of the anion exchange resin was washed in batch mode in a 3 L nalgene beaker with 4-2 L portions of 18Ω deionized water, until the effluent runs clear. The anion exchange resin was drained of water and dehydrated with ethyl lactate (three bed volumes) and stored in ethyl lactate. Dehydration was considered complete when the effluent solvent had a moisture content of less than 0.5%

EXAMPLE 3

A portion (ca 50 g) of the dehydrated chelating resin from Example 1 was added to a fritted glass funnel and partially dried by suction filtration. A 7 g portion of the dried chelating resin was measured into each of two 125 mL Nalgene bottles.

A portion (ca. 50 g) of dehydrated anion exchange resin from Example 2 was dried in the same manner, and a 14 g portion was weighed into one of the Nalgene bottles (supra). Each bottle was charged with 42 g of a 0.2 μm filtered cresolic novolak solution in ethyl lactate (ca. 37% solids by weight) and rolled for 60 minutes. At this time samples were taken of each and analyzed for metals content.

Metals	Baseline	Aix[1]	Difference	% Removal
Mixed Bed - Acid treated IRC-718 and IRA-93				
Cr	183	106	77	42.3%
Fe	95	54	41	43.2%
Na	37	60	−23	−63.0%
Mo	182	45	117	64.7%
Acid treated IRC-718 Only				
Cr	183	160	23	12.7%
Fe	95	73	22	23.0%
Na	37	296	−260	−705.4%
Mo	182	197	−15	−8.4%

[1]·After ion exchange.

These data highlight the performance difference between acid-washed IRC-718 (alone) and in 1:2 combination with IRA-93. The chelating resin alone exhibits poor Mo and Cr removal, and adds higher Na contaminant levels, whereas the mixed bed system exhibits better removal for Fe, Mo, and Cr while contaminating less for Na.

EXAMPLE 4

A batch experiment was set up as in Example 3, except that the chelating resin (from Example 1) was acid treated for 18 hours. Once dried, the chelating resin was weighed out into each of five 125 mL Nalgene bottles as follows: #1, 10 g IRC-718; #2, 10 g IRC-718; #3, 6.33 g IRC-718, #4, 5 g IRC-718; and #5, 0 IRC-718. The dried anion exchange resin was then added to the 125 mL Nalgene bottles in the

following amounts: #1, 0 IRA-93; #2, 10 g IRA-93; #3, 13.67 g IRA-93; #4, 15 g IRA-93, and #5, 10 g IRA-93. Into each of the five bottles 40 grams of an acrylate-hydroxystyrene polymer solution in ethyl lactate was added. Each bottle was agitated on rollers for 60 minutes. At this time, the bottles were removed and samples were taken for metals and chloride testing. Results are as follows:

1:0 IRC-718 to IRA-93 (in ppb)

Metal	Baseline	Aix[1]	Difference	% Reduction
Ca	15	16	−1	−5%
Zn	127	46	81	63.8%
Fe	2146	1331	815	38.0%
Na	0	109	−109	*
Mo	49	28	21	43.3%

1:1 IRC-718 to IRA-93 (in ppb)

Metal	Baseline	Aix[1]	Difference	% Reduction
Ca	15	11	5	29.6%
Zn	127	38	89	70.4%
Fe	2146	611	1535	71.5%
Na	0	14	−14	*
Mo	49	13	36	74.3%

1:2 IRC-718 to IRA-93 (in ppb) - Optimum Ratio of IX Resins

Metal	Baseline	Aix[1]	Difference	% Reduction
CA	15	9	6	38.8%
Zn	127	36	91	71.5%
Fe	2146	572	1574	73.3%
Na	0	0	0	*
Mo	49	9	40	82.0%

1:3 IRC-718 to IRA-93 (in ppb)

Metal	Baseline	Aix[1]	Difference	% Reduction
Ca	15	24	−8	−55.3%
Zn	127	51	76	59.5%
Fe	2146	635	1511	70.4%
Na	0	0	0	*
Mo	49	9	40	80.8%

0:1 IRC-718 to IRA-93 (in ppb)

Metal	Baseline	Aix[1]	Difference	% Reduction
Ca	15	16	−1	−6.7%
Zn	127	74	53	42.0%
Fe	2146	1349	797	37.1%
Na	0	10	−10	*
Mo	49	25	24	49.0%

[1] After ion exchange.

These data highlight the improved performance of the mixed bed system over either the chelating resin alone or in the anion exchange resin alone. The optimum ratio for metals reduction (supra) is one part IRC-718 to two parts IRA-93.

EXAMPLE 5

A column was prepared using ca. 500 mL of the chelating resin slurry in ethyl lactate from Example 1 and 1000 mL of

the anion exchange resin slurry in ethyl lactate from Example 2. These slurries were combined in a 3000 mL beaker and stirred with a polypropylene stirrer until a homogeneous mixture was observed. A 2" by 36" column was packed with the slurry, with stirring to maintain ion exchange resin homogeneity. In this way a total bed height of 30" was obtained. A 0.2 μm filtered cresolic novolak solution in ethyl lactate (ca. 37% solids by weight) was passed through the column at a flow rate of ca. 40 mL/min. The first three bed volumes (2300 mL) were discarded to eliminate flow inconsistencies and dilution effects. The remaining novolak solution was collected and cycled over the ion exchange resin bed a total of 4 times, with samples taken in 30 mL HDPE bottles after each pass. Results in ppb are as follows:

METAL	BIX[1]	1st PASS	2nd PASS	3rd PASS	4th PASS	Redn. (total)	% RED (total)
Cr	149	41	20	20	13	136	91
Fe	90	49	29	30	15	75	83
Na	129	54	36	55	41	88	68
Mo	212	56	35	35	30	182	86

[1] Before ion exchange.

EXAMPLE 6

The chelating and anion exchange resins from examples 1 and 2 (respectively) were dried as described in Example 3, except that ca. 150 g of each resin slurry was used. A 500 mL Nalgene bottle was charged with 42 g of the chelating resin, and 83 g of the anion exchange resin. A 250 g portion of an i-Line photoresist consisting of a naphthoquionone diazide sulfonyl halide ester and novolak resin was added, and the container was rolled for ca. 18 h. A sample was then taken and analyzed for metals content. The results in ppb are as follows:

Metal	Baseline	Aix[1]	Difference	% Reduction
Cr	79	21	58	73.8%
Fe	39	13	26	66.6%
Na	50	16	34	67.1%
Mo	41	23	18	43.3%

[1] After ion exchange.

EXAMPLE 7

A batch experiment was set up as described in Example 3, except that a single run was performed using the mixed bed system only. A 40 g portion of an i-Line photoresist consisting of a naphthoquionone diazide sulfonyl halide ester and novolak resin was added, and the container was rolled for ca. 18 h. A sample was then taken and submitted for metals testing. The results in ppb are as follows:

Metal	Baseline	Aix[1]	Difference	% Reduction
Zn	19	13	6	31.6%
Cr	45	8	37	82.0%
Fe	37	19	18	49.5%
Na	509	19	490	96.4%
Mo	33	13	20	59.6%
Ca	8	33	−25	−319%

[1] After ion exchange.

EXAMPLE 8

A column was prepared as described in Example 5 (the "homogeneous" bed). A second 2" by 36" column was

prepared (the "stratified" bed) in which ca. 500 mL of the chelating resin slurry in ethyl lactate from Example 1 was added to the column to form a lower layer, and ca. 1000 mL of the anion exchange resin slurry in ethyl lactate from Example 2 was added to the column to form an upper layer. In this way total bed heights of 30" were obtained. A 0.2 μm filtered cresolic novolak solution in ethyl lactate (ca. 37% solids by weight) was passed through each column at a flow rate of ca. 40 mL/min. The first three bed volumes (2300 mL) for each column were discarded to eliminate flow inconsistencies and dilution effects. The remaining novolak solution was collected and cycled over the respective ion exchange resin bed a total of 3 times, with samples taken in 30 mL HDPE bottles after each pass. Results in ppb are as follows:

	Stratified bed				Homogeneous bed			
	Fe	Cr	Mo	Na	Fe	Cr	Mo	Na
BASELINE	153	43	47	411	149	67	40	452
1 PASS	91	33	23	129	52	58	13	122
2 PASSES	88	35	30	139	27	52	5	127
3 PASSES	63	35	24	142	22	45	5	89
DIFFERENCE	90	8	23	269	127	22	35	361
% REDN.	58.9	18.3	49.0	65.4	85.0	32.9	86.5	80.3

Significantly better performance is seen for the homogeneous bed than for the stratified bed.

EXAMPLE 9

A portion (ca. 250 g) of the dehydrated chelating resin from Example 1 was added to a flitted glass funnel and partially dried by suction filtration. A 100 g portion of the dried chelating resin was measured into the first of two 500 ml. Nalgene bottles (the control) and a 33 g portion of the dried chelating resin was measured into the second (mixed bed).

A portion (ca. 100 g) of dehydrated anion exchange resin from Example 2 was dried in the same manner, and a 67 g portion was weighed into the second (mixed bed) Nalgene bottle (supra). Each bottle was charged with 100 g of a 0.2 mm filtered cresolic novolak solution in ethyl lactate (ca. 37% solids by weight) and rolled for 6 hours. At this time samples were taken of each and submitted for metals content and residual acid. The results (in ppb, unless otherwise indicated) are shown below.

cation exchange resin with an acid to remove essentially all metal ions therefrom and rinsing said acid washed chelating cation exchange resin with water until the water effluent has a pH varying between about 1 and 7, homogeneously admixing the chelating cation exchange resin with an anion exchange resin and contacting said organic solution containing heavy metal ions with said mixture of chelating cation exchange resin and anion exchange resin, the contact between the solution and the mixed exchange resins being for a time sufficient to reduce the concentration of said heavy metal ions contained in said organic solution.

2. The process of claim 1 where the molar ratio of base groups to acid groups in the exchange resin mixture varies between 1.2 to 10 and 1 to 1.5.

3. The process of claim 2 where the molar ratio varies between 1 to 2 and 1 to 4.

4. The process of claim 1 where the acid used to prepare the chelating cation exchange resin is a mineral acid.

5. The process of claim 4 where the acid is hydrochloric acid.

6. The process of claim 1 where the organic solution is a solution of a photoresist containing a dissolved photoactive component and an organic polymer binder.

7. The process of claim 1 where the organic solution is a solution of an antireflective coating composition containing a dye and an organic polymer.

8. The process of claim 1 where the organic solution is a solution of an organic polymer.

9. The process of claim 8 where the polymer is a novolak resin.

10. The process of claim 1 where the chelating cation exchange resin is an acrylate-divinyl benzene copolymer having hydroxamic acid groups.

11. The process of claim 1 where the anion exchange resin comprises a polyamine on a polymer backbone selected from the group consisting of polystyrene, polyacrylic acid and polyethylene imine.

12. A process for removing heavy metal ions contained in an organic solution 12. The process of claim 1 where the chelating cation exchange resin comprises a polymer substituted with aminomethyl phosphonate groups.

13. The process of claim 12 where the organic solution is of an organic resin.

14. The process of claim 13 where the resin is a novolak resin.

15. The process of claim 12 where the chelating cation exchange resin is an acrylate-divinyl benzene copolymer having hydroxamic acid groups.

METAL	BASELINE (No Ion exchange)	CONTROL (IRC-718)	CONTROL % REDUCTION (From Baseline)	MIXED BED (-718 & -93)	MIXED BED % REDUCTION (From Baseline)
Na	101	453	–349%	75	25%
Fe	75	29	61%	41	46%
Mo	230	105	54%	39	83%
Cr	153	88	43%	79	49%
Acid*	<0.002	0.02	NA	<0.002	NA

*Acid Results are reported in pans per thousand; metals results are reported in parts per billion (ppb).

Results show best performance in metal reduction overall with the mixed bed, with no detectable acid residues.

We claim:

1. A process for removing heavy metal ions contained in an organic solution of one or more photoresist or antireflective components while inhibiting introduction of acid into solution, said process comprising the steps of providing a chelating cation exchange resin, washing said chelating

16. A process for removing heavy metal ions contained in an organic solution containing dissolved heavy metal ions while minimizing acid introduction into the solution, said process comprising the steps of contacting said organic solution with a homogenous mixture of a chelating cation exchange resin washed with an acid and an anion exchange resin, the contact between the solution and the exchange resin mixture being for a time sufficient to reduce the

concentration of said heavy metal ions contained in said organic solution and the contact with the anion exchange resin being for a time sufficient to remove all acid residues within said organic solution and generated by contact of the solution with the chelating cation exchange resin.

17. The process of claim 16 including the step of washing said acid washed chelating exchange resin with water until the water effluent has a pH varying between about 1 and 7 prior to contacting said organic solution with said chelating cation exchange resin.

18. The process of claim 16 where the molar ratio of base groups to acid groups in the exchange resin mixture varies between 1.2 to 10 and 1 to 1.5.

19. The process of claim 18 where the molar ratio varies between 1 to 2 and 1 to 4.

20. The process of claim 16 where the acid used to prepare the chelation cation exchange resin is hydrochloric acid.

*   *   *   *   *

United States Patent [19]

Thackeray et al.

[11] **Patent Number:** **5,851,738**

[45] **Date of Patent:** **Dec. 22, 1998**

[54] **METHOD COMPRISING SUBSTRATES COATED WITH AN ANTIHALATION LAYER THAT CONTAINS A RESIN BINDER COMPRISING ANTHRACENE UNITS**

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[73] Assignee: **Shipley Company, L.L.C.**, Marlborough, Mass.

[21] Appl. No.: **978,688**

[22] Filed: **Nov. 26, 1997**

Related U.S. Application Data

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[51] **Int. Cl.⁶** **G03C 5/16**; C08J 3/28

[52] **U.S. Cl.** **430/327**; 430/325; 430/326; 430/330; 522/113; 522/126; 522/130; 522/132; 522/133

[58] **Field of Search** 430/271.1, 156, 430/325, 327, 330, 510, 512, 326; 522/113, 126–133

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Primary Examiner—Bernard Codd
Attorney, Agent, or Firm—Robert L. Goldberg; Peter F. Corless; Darryl P. Frickey

[57] **ABSTRACT**

Antihalation compositions and methods for reducing the reflection of exposure radiation of a photoresist overcoated said compositions. The antihalation compositions of the invention comprise a resin binder and material capable of causing a thermally induced crosslinking reaction of the resin binder.

29 Claims, 1 Drawing Sheet
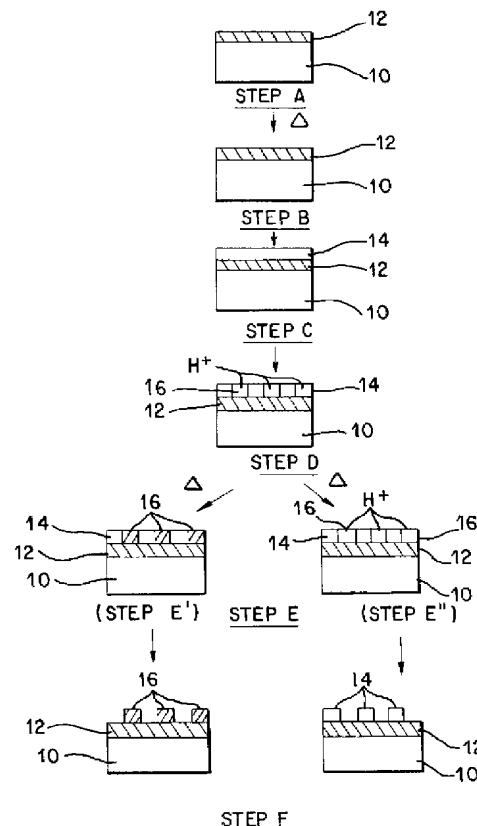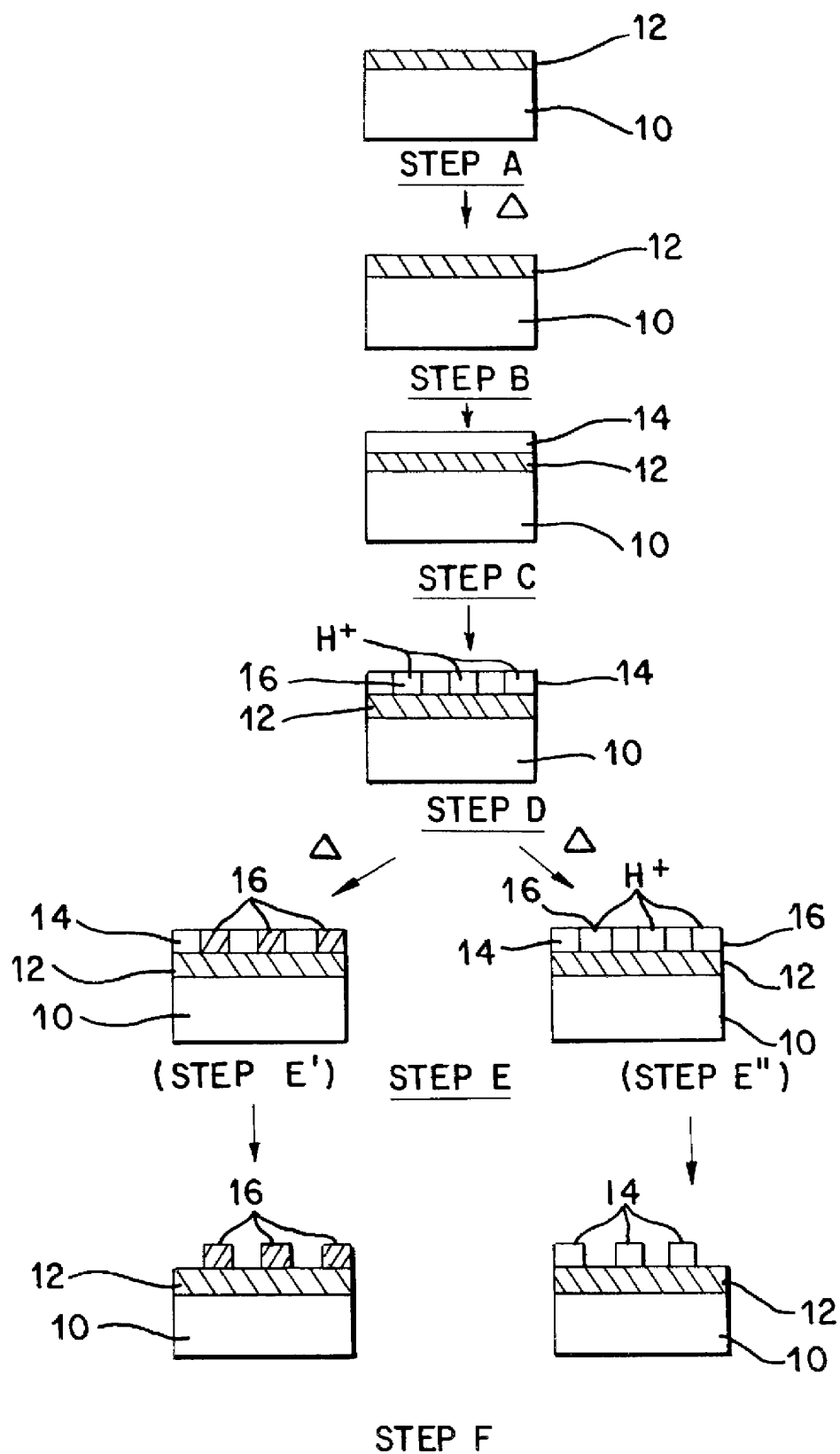
STEP F

12

10

STEP A

Δ

12

10

STEP B

14

12

10

STEP C

H⁺

16

12

14

10

STEP D

Δ   Δ

16

14

12

10

(STEP E') STEP E (STEP E'')

16

H⁺

14

16

12

10

16

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STEP F

14

12

10

1

METHOD COMPRISING SUBSTRATES COATED WITH AN ANTIHALATION LAYER THAT CONTAINS A RESIN BINDER COMPRISING ANTHRACENE UNITS

This is a divisional of application Ser. No. 07/792,482 filed on Nov. 15, 1991.

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to compositions that reduce the reflection of exposure radiation from a substrate back to an overcoated resist layer. More particularly, the invention relates to an antihalation composition characterized in one aspect by containing a thermally activated crosslinking agent.

2. Background Art

Photoresists are used for transfer of an image to a substrate. A coating layer of a photoresist is formed on a substrate, and the resist layer is then selectively exposed through a photomask to a source of activating radiation. The photomask has areas that are opaque to activating radiation and other areas that are transparent to activating radiation. Exposure to activating radiation provides a photoinduced chemical transformation of the photoresist coating to thereby transfer the pattern of the photomask to the resist coated substrate. Following exposure, the photoresist is developed to provide a relief image that permits selective processing of the substrate.

A photoresist can be either positive-acting or negative-acting. For most negative photoresists, those coating layer portions that are exposed to activating radiation polymerize or crosslink in a reaction between a photoactive compound and polymerizable reagents of the resist composition. Consequently, the exposed coating portions are rendered less soluble in a developer solution than unexposed portions. For a positive-acting photoresist, exposed portions are rendered more soluble in a developer solution while areas not exposed remain comparatively less developer soluble. The background of photoresists are described by Deforest, *Photoresist Materials and Processes*, McGraw Hill Book Company, New York, ch. 2, 1975, and by Moreay, *Semiconductor Lithography, Principles, Practices and Materials*, Plenum Press, New York, ch. 2 and 4, both incorporated herein by reference for their teaching of photoresists and methods of making and using same.

A major use of photoresists is in semiconductor manufacture where an object is to convert a highly polished semiconductor slice, such as silicon or gallium arsenide, into a complex matrix of electron conducting paths, preferably of micron or submicron geometry, that perform circuit functions. Proper photoresist processing is a key to attaining this object. While there is a strong interdependency among the various photoresist processing steps, exposure is believed to be one of the most important steps in attaining high resolution photoresist images.

Reflection of the activating radiation used to expose a photoresist often poses notable limits on resolution of the image patterned in the resist layer. Reflection of radiation from the substrate/resist interface can produce variations in the radiation intensity in the resist during exposure, resulting in non-uniform photoresist linewidth upon development. Radiation also can scatter from the substrate/resist interface into regions of the resist where exposure is not intended, again resulting in linewidth variations. The amount of scattering and reflection will typically vary from region to region, resulting in further linewidth non-uniformity.

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Reflection of activating radiation also contributes to what is known in the art as the "standing wave effect". To eliminate the effects of chromatic aberration in exposure equipment lenses, monochromatic or quasimonochromatic radiation is commonly used in resist projection techniques. Due to radiation reflection at the resist/substrate interface, however, constructive and destructive interference is particularly significant when monochromatic or quasi-monochromatic radiation is used for photoresist exposure. In such cases the reflected light interferes with the incident light to form standing waves within the resist. In the case of highly reflective substrate regions, the problem is exacerbated since large amplitude standing waves create thin layers of underexposed resist at the wave minima. The underexposed layers can prevent complete resist development causing edge acuity problems in the resist profile. The time required to expose the photoresist is generally an increasing function of resist thickness because of the increased total amount of radiation required to expose an increased amount of resist. However, because of the standing wave effect, the time of exposure also includes a harmonic component which varies between successive maximum and minimum values with the resist thickness. If the resist thickness is non-uniform, the problem becomes more severe, resulting, in variable linewidth control.

Variations in substrate topography also give rise to resolution-limiting reflection problems. Any image on a substrate can cause impinging radiation to scatter or reflect in various uncontrolled directions, affecting the uniformity of resist development. As substrate topography becomes more complex with efforts to design more complex circuits, the effects of reflected radiation become more critical. For example, metal interconnects used on many microelectronic substrates are particularly problematic due to their topography and regions of high reflectivity.

Such radiation reflection problems have been addressed by the addition of certain dyes to photoresist compositions, the dyes absorbing radiation at or near the wavelength used to expose the photoresist. Exemplary dyes that have been so employed include the coumarin family, methyl orange and methanil yellow. Some workers have found that use of such dyes can limit resolution of the patterned resist image.

Another approach has been to use a radiation absorbing layer interposed between the substrate surface and the photoresist coating layer. See, for example, PCT Application WO 90/03598, and U.S. Pat. Nos. 4,910,122, 4,370,405 and 4,362,809, all of which are incorporated herein by reference for their teaching of antireflective (antihalation) compositions and use of the same. At least some prior antireflective coatings, however, suffer from poor adhesion to the to overcoated photoresist layer and/or the underlying substrate surface. Such adhesion problems can severely compromise the resolution of the patterned photoresist image.

Thus, it would be desirable to have an antihalation coating composition that absorbs significantly incident and reflective exposure radiation, and that provides substantial standing wave attenuation. It would be further desirable to have an antihalation composition that can be coated on a microelectronic substrate and adhere well to both a subsequently applied photoresist coating layer and the underlying substrate surface.

SUMMARY OF THE INVENTION

The present invention provides an antihalation composition suitable for use with a photoresist, the antihalation composition in general comprising a resin binder and a

compound capable of causing a thermally induced crosslinking reaction of the resin binder. Components of the antihalation composition preferably can crosslink with an overcoated layer of the photoresist composition, thereby increasing adhesion between the two coating layers and avoiding notable problems of at least some prior antireflective systems. The antihalation compositions of the invention may further comprise an acid or acid generator compound to catalyze the reaction between the resin binder and the crosslinking compound, enabling the crosslinking reaction to proceed at relatively lower temperatures. As used herein, the term acid generator refers to a compound that generates an acid upon appropriate treatment of the compound, for example, upon exposure to activating radiation or thermal treatment. The thermally active crosslinker can be a variety of materials and, preferably, is an amine-based material such as a benzoguanamine-based or melamine-based resin. To enhance radiation absorption properties, the antihalation compositions of the invention may further include one or more dye compounds that absorb radiation at or near the exposure wavelength of the overcoated photoresist.

The invention further provides a method for application and use of the antihalation coating composition with a photoresist. Thus, in a preferred aspect, a method is provided comprising (a) applying a layer of an antihalation composition of the invention on a substrate; (b) at least partially curing the antihalation coating layer; (c) applying a layer of a photoresist on the coated substrate; (d) exposing selected portions of the photoresist layer; (e) baking the applied antihalation and photoresist coating layers; and (f) developing the exposed photoresist layer. When a suitable photoresist is employed, baking of the two coating layers results in crosslinking between components of the antihalation and photoresist compositions, thereby providing excellent adhesion between the two coating layers. It has also been found that the antihalation compositions of the invention adhere well to substrate surfaces, including substrates used in microelectronic applications.

The invention further provides methods for forming a relief image and novel articles of manufacture consisting of substrates coated with an antihalation composition of the invention alone or in combination with a photoresist composition. In particular, a coated substrate is provided, the substrate having an antihalation composition of the invention coated thereon, and a photoresist coated over said antihalation composition, the photoresist comprising a resin binder and a radiation sensitive component.

BRIEF DESCRIPTION OF THE DRAWING

The FIGURE illustrates schematically processes of the invention.

DETAILED DESCRIPTION OF THE INVENTION

A preferred antihalation composition of the invention comprises a mixture of materials that will crosslink, cure or harden upon thermal treatment. More particularly, a preferred composition comprises a resin binder and a material capable of undergoing a thermally induced crosslinking reaction with said resin binder. Preferably the resin binder and the thermal crosslinking compound are materials which, in an uncured state, are soluble in a nonreactive solvent or solvent mixture and are capable of forming a homogeneous, nontacky, adherent film on a substrate surface onto which it is applied.

A particularly preferred antihalation composition comprises an amine-based thermal crosslinker and a phenol-

based resin binder. Suitable amine-based thermal crosslinkers include melamine-formaldehyde resins, glycoluril-formaldehyde resins, and urea-based resins. Suitable melamine resins include the melamine resins manufactured by American Cyanamid Company of Wayne, N.J. and sold under the trade names Cymel® 300, 301, 303, 350, 370, 380, 1116 and 1130. Suitable glycoluril resins include those sold by the American Cyanamid Company under the trade names of Cymel® 1170, 1171, 1172. Suitable urea-based resins include those sold by the American Cyanamid Company under the trade names of Beetle® 60, 65 and 80. A particularly preferred amine-based crosslinker is a benzoguanamine-based material, including the benzoguanamine resins sold by the American Cyanamid Company under the trade names of Cymel® 1123 and 1125. Additionally, combinations of the above amine-based crosslinkers will be suitable, including combinations that comprise a benzoguanamine-based material. In addition to the above resins available from the American Cyanamid Company, a large number of similar resins are commercially available from other suppliers. Additionally, such amine-based resins may be prepared by the reaction of acrylamide or methacrylamide copolymers with formaldehyde in an alcohol-containing solution, or alternatively by the copolymerization of N-alkoxymethyl acrylamide or methacrylamide with other suitable monomers. The crosslinker component of the antihalation compositions of the invention in general are used in an amount of between about 5 and 50 weight percent of total solids of the composition, more typically in amount of 30 weight percent of total solids of the composition.

As noted above, the amine-based crosslinker compound of the antihalation composition is preferably used in combination with a phenol-based resin binder. Suitable phenol-based resin binders include, for example, novolak resins; poly(vinylphenols) and copolymers of the same with styrene, alpha-methylstyrene; acrylic resins; polyglutarimides; polyacrylic acid or polymethacrylic acid copolymers; alkali-soluble polyacrylamides and polymethacrylamide copolymers; copolymers containing 2-hydroxyethylmethacrylate and 2-hydroxypropylmethacrylate; polyvinyl alcohols such as those prepared from partially hydroxylated polyvinyl acetates; alkali-soluble styrene-allyl alcohol copolymers; and mixtures thereof.

Of the above, poly(vinylphenol) and its copolymers and novolak resins containing hydroxyl groups and sites for the electrophilic substitution of aromatic rings at positions ortho- or para- relative to the hydroxyl group are preferred. Novolak resins that are useful in conjunction with amine-based resins in the acid hardening resin system are alkali-soluble film forming phenolic resins having a molecular weight (weight average) ranging from about 300 to about 100,000 daltons, and preferably from about 1000 to 20,000 daltons. These novolak resins may be prepared by the condensation reaction of a phenol, a naphthol or a substituted phenol, such as, cresol, xylenol, ethylphenol, butylphenol, oxypropyl methoxyphenol, chlorophenol, bromophenol, resorcinol, naphthol, chloronaphthol, bromonaphthol or hydroquinone with formaldehyde, acetaldehyde, benzaldehyde, furfural acrolein, or the like. Blends of suitable novolak resins may also be used in order to adjust the dissolution rate of the exposed coating in aqueous base solutions as well as for adjusting the viscosity, hardness and other physical properties of the coating. Suitable novolak resins are disclosed in numerous patents including U.S. Pat. Nos. 3,148,983; 4,404,357; 4,115,128;

4,377,631; 4,423,138; and 4,424,315, the disclosures of which are incorporated by reference herein.

Poly(vinylphenols) are thermoplastic materials that may be formed by block polymerization, emulsion polymerization or solution polymerization of corresponding monomers in the presence of a cationic catalyst. Vinylphenols used for the production of poly(vinylphenol) resins may be prepared, for example, by hydrolysis of commercially available coumarins or substituted coumarins, followed by decarboxylation of the resulting hydroxy cinnamic acids. Useful vinyl phenols also may be prepared by dehydration of the corresponding hydroxy alkyl phenol or by decarboxylation of hydroxy cinnamic acids resulting from the reaction of substituted or non-substituted hydroxy benzaldehydes with malonic acid. Preferred poly(vinylphenol) resins prepared from such vinyl phenols have a molecular weight range of from about 2,000 to about 100,000 daltons. Procedures for the formation of poly(vinylphenol) resins can be found in U.S. Pat. No. 4,439,516, incorporated herein by reference.

Another suitable phenol-based resin binder for use in the antihalation compositions of the invention are copolymers of phenolic units and cyclic alcohol units analogous in structure to novolak resins and poly(vinylphenol) resins. Such copolymers are described in U.S. patent application Ser. No. 07/354,800, incorporated herein by reference. These copolymers may be formed in several ways. For example, in the conventional preparation of a poly(vinylphenol) resin, a cyclic alcohol may be added to the reaction mixture as a comonomer during the polymerization reaction which is thereafter carried out in a normal manner. The cyclic alcohol is preferably aliphatic, but may contain one or two double bonds. The cyclic alcohol is preferably one closest in structure to the phenolic unit. For example, if the resin is a poly(vinylphenol), the comonomer would be vinyl cyclohexanol.

The preferred method for formation of the copolymer comprises hydrogenation of a preformed poly(vinylphenol) resin. Hydrogenation may be carried out using art recognized hydrogenation procedures, for example, by passing a solution of the phenolic resin over a reducing catalyst such as a platinum or palladium coated carbon substrate or preferably over Raney nickel at elevated temperature and pressure. The specific conditions are dependent upon the polymer to be hydrogenated. More particularly, the polymer is dissolved in a suitable solvent such as ethyl alcohol or acetic acid, and then the solution is contacted with a finely divided Raney nickel catalyst at a temperature of from about 100° to 300° C. at a pressure of from about 50 to 300 atmospheres or more. The finely divided nickel catalyst may be a nickel-on-silica, nickel-on-alumina, or nickel-on-carbon catalyst depending on the resin to be hydrogenated.

Another suitable resin binder for the antihalation compositions of the invention is a polymer comprising anthracene units. This polymer may contain other units such as carboxy and/or alkyl ester units pendant from the polymer backbone. In particular, a preferred resin binder has a structure of formula (I):
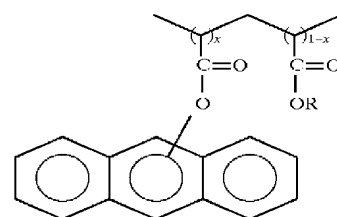
wherein R is a hydrogen or an alkyl group (e.g., an alkyl group having from 1 to 6 carbon atoms); and x is the mole fraction of anthracene ester units in the polymer, and wherein x is suitably a value of from 0.1 to 1.0. The anthracene groups may be unsubstituted or substituted at one or more available positions by substituents such as, for example, halo, alkoxy and alkyl. Suitably the anthracene moiety can be substituted to a carboxyl group at any available position of the anthracene ring, as shown above in formula (I). Preferably, the resin binder contains 9-anthracene ester units. These anthracene resin binders can be prepared, for example, by condensation of anthranol with methacryloyl chloride, followed by condensation of the vinyl anthracene ester reaction product to form the homopolymer, or condensation of the vinyl ester reaction product with other polymerizable compounds to form a mixed polymer.

For enhanced etch resistance of the antihalation composition, a silicon-containing material can be employed, such as poly(vinylsilsesquioxane). Such a silicon-containing resin can be used as the sole resin binder of the composition, or in combination with other resin binders, such as the phenolic resins described above.

The concentration of the resin binder component of the antihalation compositions of the invention may vary within relatively broad ranges, and in general the resin binder is employed in a concentration of from about 50 to 95 weight percent of the total of the dry components of the composition, more typically from about 60 to 80 weight percent of the total dry components.

As indicated above, the antihalation compositions of the invention may further comprise an acid or acid generator compound for catalyzing the crosslinking reaction between the resin binder and crosslinker compound. Preferably an acid generator compound is employed. Suitable acid generator compounds include compounds that liberate acid upon photolysis or thermal treatment. Preferably a thermal acid generator is employed, i.e., a compound that generates acid upon thermal treatment. A variety of known thermal acid generator compounds are suitably employed in the antireflective compositions of the invention such as, for example, 2,4,4,6-tetrabromocyclohexadienone, benzoin tosylate, 2-nitrobenzyl tosylate, and alkyl esters of organic sulfonic acids. Typically a thermal acid generator is present in an antihalation composition in concentration of from about 1 to 15 percent by weight of the total of the dry components of the composition, more preferably about 5 percent by weight of the total dry components. Photoacid generators may also be employed in an antihalation composition, for example onium salts, halogenated non-ionic photoacid generators such as 1,1-bis[p-chlorophenyl]-2,2,2-trichloroethane, and other photoacid generators disclosed herein for use in photoresist compositions. Suitable amounts of a photoacid generator in an antihalation composition in general range from about 1 to 15 percent by weight of the total of dry components of the composition. For an antihalation composition containing a photoacid generator, a coating layer of the composition is exposed to

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an effective amount of activating radiation to generate the photoacid, followed by a post-exposure bake at a temperature sufficient to at least partially cure the coating layer.

It should be appreciated that an antihalation composition of the invention can be non-photoimageable, e.g., by not employing an acid catalyst or employing a non-photoactive acid catalyst such as a thermal acid generator; or an antihalation composition can be rendered photoimageable (and hence developable) by incorporating an effective amount of a suitable photoacid generator into the composition and then exposing a coating layer of the composition through a photomask. Suitable photoacid generators include the non-ionic halogenated photoacid generators as described herein.

Another optional additive of the compositions of the invention are compounds that serve as dyes and absorb radiation used to expose an overcoated photoresist layer. The dye should absorb well at the wavelength at which the overcoated photoresist is exposed and, therefore, selection of a suitable dye for a specific antihalation composition in large part will be determined by the particular photoresist that is employed. For example, if an antireflective composition is used in combination with a deep U.V. photoresist (i.e., a resist that is exposed at between 100 and 300 nm), the dye compound should strongly absorb in the deep U.V. region. Suitable dyes are known in the art and include, for example, the curcumin family and derivatives thereof, anthracene, anthrarobin, Sudan-orange, benzophenothiazine and naphthol-AS. Typically a dye is present in an antihalation composition in a concentration of from about 2 to 30 percent by weight of the total of the dry, components of the composition, more preferably from 5 to 15 percent by weight of the total dry components.

Other optional additives include surface leveling agents, for example, the leveling agent available under the tradename Silwet 7604 from Union Carbide.

To make a liquid coating composition, the components of the antihalation composition are dissolved in a suitable solvent such as, for example, one or more of the glycol ethers such as 2-methoxyethyl ether (diglyme), ethylene glycol monomethyl ether, and propylene glycol monomethyl ether; N-methyl pyrrolidinone; esters such as methyl cellosolve acetate, ethyl cellosolve acetate, propylene glycol monomethyl ether acetate, dipropylene glycol monomethyl ether acetate and other solvents such as dibasic esters, propylene carbonate and gamma-butyro lactone. The concentration of the dry components in the solvent will depend on several factors such as the method of application. In general, the solids content of an antihalation composition varies from about 1 to 50 weight percent of the total weight of the antihalation composition, preferably the solids content varies from about 5 to 35 weight percent of the total weight of the antihalation composition.

A variety of photoresist compositions can be employed with the antihalation compositions of the invention. Preferably, a photoresist is employed that, when coated over a film layer of antihalation composition, is capable of crosslinking with the lo antihalation composition at the interface of the two coating layers. More specifically, preferred photoresists for use with the antihalation compositions of the invention include positive-acting and negative-acting photoacid-generating compositions that comprise a resin system that can crosslink with one or more components of the antihalation composition.

A particularly preferred group of photoresists for use with the compositions of the invention comprise a radiation sensitive component such as aphotoacid generator compound and a mixture of materials that will cure, crosslink or

harden upon heating and exposure to acid. A preferred mixture comprises a phenol-based resin binder and an amine-based crosslinker. Suitable phenol-based resins include novolak resins, poly(vinylphenols) and various copolymers thereof. Suitable amine-based crosslinkers include those described above for the antihalation compositions, in particular the melamine-formaldehyde Cymel resins available from American Cyanamid. Suitable photoacid generator compounds include the onium salts, such as those disclosed in U.S. Pat. Nos. 4,442,197, 4,603, 101, and 4,624,912, each incorporated herein by reference; and non-ionic organic photoactive compounds such as the halogenated photoactive compounds disclosed in the below referenced European Patent Applications. These photoactive compounds should be present in a photoresist in an amount sufficient to enable development of a coating layer of the resist following exposure to activating radiation. Preferred negative-acting photoresists for use in accordance with the invention include the acid-hardening photoresists as disclosed, for example, in European Patent Applications Nos. 0401499 and 0423446, both incorporated herein by reference. As used herein, the term "acid-hardening photoresist" refers to photoresist compositions of the general type described above and in these referenced European Patent Applications.

Other preferred photoresists include positive-acting photoresists that contain components that can crosslink with one or more components of the antihalation compositions of the invention. Such photoresists suitably comprise a phenol-based resin binder in combination with a radiation sensitive component. Suitable resin binders include novolak resins, poly(vinylphenols) and various copolymers thereof. Suitable radiation sensitive components can comprise a variety of photoacid generator compounds including the naphthoquinone diazide sulfonic acid esters such as 2,1,4-diazonaphthoquinone sulfonic esters and 2,1,5-diazonaphthoquinone sulfonic acid esters; the onium salts; and other known acid generators such as those disclosed in European Patent Application Nos. 0164248 and 0232972, both incorporated herein by reference. In addition to "conventional" positive-acting resists, chemically amplified positive resists are particularly suitable for use with the antihalation compositions of the invention. As with the above described acid-hardening resists, a chemically amplified positive resist generates a catalytic photoproduct upon exposure to activating radiation. In a positive system, this photoproduct (e.g., acid) renders the exposed regions of the resist more developer soluble, for example by catalyzing a deprotection reaction of one or more of the resist components to liberate polar functional groups such as carboxy. See, Lamola, et al., "Chemically Amplified Resists", *Solid State Technology*, 53–60 (August 1991), incorporated herein by reference.

Reference is now made to the FIGURE of the Drawing which shows a preferred method for use of an antihalation composition of the invention. In Step A, an antihalation composition is applied to substrate 10 to provide antihalation coating layer 12. The antihalation composition may be applied by virtually any standard means including spin coating. The antireflective composition in general is applied on a substrate with a dried layer thickness of between about 0.05 and 0.5 μm, preferably a dried layer thickness of between about 0.10 and 0.20 μm. The substrate is suitably any substrate conventionally used in processes involving photoresists. For example, the substrate can be silicon, silicon dioxide or aluminum—aluminum oxide microelectronic wafers. Gallium arsenide, ceramic, quartz or copper

substrates may also be employed. Substrates used for liquid crystal display applications are also suitably employed, for example glass substrates, indium tin coated substrates and the like.

In Step B the antihalation layer is at least partially cured. Cure conditions will vary with the components of the antireflective composition. Thus, if the composition does not contain an acid catalyst, cure temperatures and conditions will be more vigorous than those of a composition containing an acid or acid generator compound. For example, for a composition containing a novolak resin binder and the benzoquanamine-formaldehyde resin Cymel 1123 as a crosslinker, typical cure conditions are heating at about 200° C. for about 30 minutes. If the thermal acid generator 2,4,4,6-tetrabromocyclohexadienone is added to this composition, cure temperatures of about 150° C. for about 30 minutes will be suitable for at least partially curing the composition coating layer. Cure conditions preferably render coating layer 12 substantially developer insoluble. Additionally, as discussed above, if the antihalation composition includes a photoacid generator, the composition coating layer can be at least partially cured by exposing the coating layer to an effective amount of activating radiation (e.g., between about 10 to 300 mJ/cm^2), followed by a post-exposure bake of from 50° to 140° C.

In Step C a photoresist is applied over the surface of the crosslinked antihalation layer 12. As with application of the antihalation composition, the photoresist can be applied by any standard means such as by spinning, dipping or roller coating. When spin coating, the solids content of the photoresist composition can be adjusted to provide a desired film thickness based upon the specific spinning equipment utilized, the viscosity of the solution, the speed of the spinner and the amount of time allowed for spinning. Following application, the photoresist coating layer 14 is typically dried by heating to remove solvent preferably until layer 14 is tack free. Optimally, no intermixing of the antihalation layer and photoresist layer should occur.

In Step D coating layer 14 is imaged with activating radiation through a mask in conventional manner. The exposure energy is sufficient to effectively activate the photoactive component of the radiation sensitive system to produce a patterned image 16 in coating layer 14 and, more specifically, the exposure energy typically ranges from about 10 to 300 mJ/cm^2, dependent upon the exposure tool.

Step E is an optional step and is employed if the photoresist requires post-exposure heating to create solubility differences between exposed and unexposed regions of a coating layer. For example, acid-hardening photoresists typically require post-exposure heating to induce the acid-catalyzed crosslinking reaction, as depicted in Step E'; and many chemically amplified positive-acting resists require post-exposure heating to induce an acid-catalyzed deprotection reaction as shown in Step E". Typically the coated substrate 10 is subjected to a post-exposure bake at temperatures of from about 50° C. or greater, more specifically a temperature in the range of from about 50° C. to 140° C.

In Step F, the exposed resist coating layer 14 is developed, preferably with an aqueous based developer such as an inorganic alkali exemplified by sodium hydroxide, potassium hydroxide, sodium carbonate, sodium bicarbonate, sodium silicate, sodium metasilicate, aqueous ammonia or the like. Alternatively, organic developers can be used such as choline based solutions; quaternary ammonium hydroxide solutions such as a tetra-alkyl ammonium hydroxide solution; various amine solutions such as ethyl amine, n-propyl amine, diethyl amine, di-n-propyl amine, triethyl amine or, methyldiethyl amine; alcohol amines such as diethanol amine or triethanol amine; cyclic amines such as pyrrole, piperidine, etc. In general, development is in accordance with art recognized procedures.

Following development, a final bake of an acid-hardening photoresist is often employed at temperatures of from about 100° to 150° C. for several minutes to further cure the developed exposed areas 16.

The developed substrate may then be selectively processed on those substrate areas bared of photoresist, for example chemically etching or plating substrate areas bared of photoresist in accordance with procedures well known in the art. Suitable etchants include a hydrofluoric acid etching solution and a plasma gas etch such as an oxygen plasma etch. In particular, a plasma gas etch readily penetrates the crosslinked antihalation coating layer.

It should be appreciated that the same removal chemistry can be employed to strip both an antihalation composition of the invention and many photoresists used, in combination therewith. For example, an acid-hardening photoresist used in combination with a preferred antihalation composition of the invention comprising a phenol-based resin binder and an amine-based crosslinker as described above, is readily stripped with a single stripper solution after selective substrate treatment. For removing such coating layers, a preferred stripper solution contains about 90 weight percent dimethylsulfoxide and 10 weight percent para-toluenesulfonic acid. Preferably this composition is used at about 70° to 90° C.

The following examples are presented to better illustrate the invention, but are not to be construed as limiting the invention to the specific embodiments disclosed. In the antihalation compositions disclosed in the examples, the novolak resin component was a formaldehyde-phenol condensate, the phenol component being 95 weight percent cresol and 5 weight percent ethylphenol, and the resin having a molecular weight (weight average) of about 11,000 daltons and a dispersity of about 20.

EXAMPLE 1

A preferred antihalation composition was prepared by mixing the components set forth below, with component amounts expressed as parts by weight:

Component	Amount
Resin binder Novolak resin	5.59
Crosslinker material Hexamethoxymethylmelamine (obtained from American Cyanamid)	1.67
Thermal acid generator 2,4,4,6-tetrabromocyclohexadienone	0.28
Surface leveling agent Silwet 7604 (obtained from Union Carbide)	0.015
Solvent	
diglyme	33.96
anisole	11.31

This antihalation composition was examined to determine the curing temperature necessary to render a film layer of the composition insoluble in aqueous developer. The solution was spin coated at 4000 r.p.m. onto seven vapor-primed (HMDS vapor, room temperature and pressure, 3 minutes) 4 inch silicon wafers. These wafers were softbaked for 60 seconds on a vacuum hotplate, each wafer baked at different temperatures, specifically each wafer was baked at 20° C.

temperature increments in a range of from 80°–200° C. Film thickness was determined from seven measurements on a Nanometrics Nanospec 215 using a refractive index of 1.64. The seven wafers were batch-developed for 60 seconds in room temperature Microposit® MF-321 developer (an aqueous tetramethylammonium hydroxide (TMAH) solution available from Shipley Co., Newton, Mass.) at a normality of 0.21 and then again measured for film thickness again, as described above using a Nanospec 215. It was found that a bake temperature of 120° C. or greater was sufficient to crosslink the antihalation coating layer so as to make it insoluble in the 0.21N TMAH developer.

EXAMPLE 2

The antihalation composition of Example 1 was tested for absorbance in the deep U.V. region. The composition was spin-coated at 3000 r.p.m. onto a 3-inch quartz wafer and softbaked at 120° C. for 60 seconds on a vacuum hotplate. Thickness was estimated by coating a 4 inch silicon wafer under the same conditions and measuring its thickness on a Nanospec 215, as described in Example 1 above. The coated wafer was analyzed on a Hewlett-Packard HP8452A UV-Visible Spectrophotometer and then corrected for the absorbance of the quartz wafer. At an exposure wavelength of 248 nm, the formulation was found to have an absorbance of 1.371 absorbance units per micron of thickness.

EXAMPLE 3

The antihalation composition of Example 1 was coated at 3000 r.p.m. onto 4 vapor-primed (HMDS, by procedures described in Example 1) 4 inch silicon wafers; the wafers were softbaked for 60 seconds on a vacuum hotplate. Two wafers were baked at 140° C., and the other two wafers were baked at 160° C. The four wafers were then each overcoated with Megaposit SNR248-1.0 deep UV photoresist (an acid-hardening photoresist sold by the Shipley Co.), using a 30 second spin at 3660 r.p.m., followed by a 60 second softbake at 90° C. on a vacuum hotplate in order to generate a resist layer thickness of approximately 1.025 microns. The wafers were exposed on a GCA Laserstep excimer laser stepper operating at the wavelength of 248 nm; an 8×8 array of patterns was utilized, covering a wide range of both exposure and focus to ensure that the optimum exposure was attained. The wafers were split up into two groups, each group containing one coated wafer cured at 140° C., and another coated wafer cured at 160° C.; one group of wafers was processed with a 60 second vacuum hotplate post-exposure bake at 110° C. while the other group was baked at 140° C. All of the wafers were developed with 0.14N TMAH MF-319 developer (Shipley Co.) in double puddle mode, using 25 and 50 second puddles and a total developer contact time of 100 seconds. Well resolved lines/spaces (including lines having essentially vertical sidewalls) of down to 0.34 μm were patterned on the antihalation coating layer.

EXAMPLE 4

Another preferred antihalation composition was prepared by mixing the components set forth below, with component amounts expressed as parts by weight:

Component	Amount
Resin binder	3.462
Novolak	
Crosslinker material	1.039
Ethylated/methylated benzoguanamine-	
formaldehyde resin (sold under the	
tradename Cymel 1123 by American Cyanamid)	
Solvent	25.500
Diethyleneglycoldimethylether	

This antihalation composition was spin coated at 4600 r.p.m. onto vapor-primed (HMDS, room temperature and pressure, 3 minutes) 4 inch silicon wafers and unprimed 4 inch quartz wafers; each wafer was softbaked at 125° C. for 60 seconds on a vacuum hotplate. The wafers were then baked for 30 minutes in a Blue M convection oven. Thickness analysis of the antihalation composition coated silicon wafers on a Nanometrics Nanospec 215 showed an average film thickness of 1733 angstroms. The quartz wafers were analyzed on a Cary3 UV-Visible Spectrophotometer; after correcting for the absorbance of the quartz wafer, the absorbance of the 1733 angstroms thick antihalation coated quartz wafer was found to be 0.719 (absorbance units) at the wavelength of 248 nm. Next, one coated silicon wafer was overcoated with Megaposit® SNR248-1.0 photoresist, and another coated silicon wafer was overcoated with Microposit® XP-89131 photoresist, both said photoresists available from the Shipley Co. The coating of the Megaposit SNR248 resist required a 30 second spin at 3680 r.p.m. and a 60 second softbake at 90° C. on a vacuum hotplate in order to generate a thickness of approximately 1.014 microns, whereas the Microposit XP-89131 resist utilized a 3760 r.p.m. spin and a 110° C. softbake temperature to achieve a coating layer thickness 1.017 microns. The two wafers were exposed on a GCA Laserstep excimer laser stepper operating at the wavelength of 248 nm; a 7-by-15 array of patterns was utilized, covering a wide range of both exposure and focus to ensure that the optimum exposure was attained. All of the wafers were post-exposure baked at 130° C. for 60 seconds on a vacuum hotplate and then developed with XP-89114 developer aqueous (TMAH developer available from the Shipley Co.) in double puddle mode, using 25 and 50 second puddles and a total developer contact time of 100 seconds. Well resolved lines/spaces (including lines having essentially vertical sidewalls) of down to 0.36 μm were patterned on the antihalation coating layer.

The foregoing description of the invention is merely illustrative thereof, and it is understood that variations and modifications can be effected without departing from the scope or spirit of the invention as set forth in the following claims.

What is claimed is:

1. A method for forming a relief image on a substrate, the method comprising:

applying on the substrate a layer of an antihalation composition comprising a resin binder and a crosslinker, the resin binder having anthracene units therein and the resin binder capable of reacting with the crosslinker, and the crosslinker capable of causing a thermally-activated crosslinking reaction of the resin binder,

applying over said antihalation composition layer a layer of a photoresist composition comprising a resin binder and a radiation senstive component, and

imagewise exposing the photoresist composition layer to activating radiation and developing the exposed photoresist composition layer.

2. The method of claim **1** where the resin binder of the antihalation composition is a copolymer.

3. The method of claim **1** where the resin binder of the antihalation composition conforms to the formula:
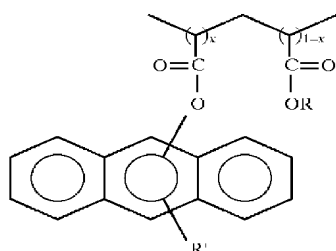
where x varies between 0.1 and 1.0, R is hydrogen or alkyl and R' is a member selected from the group consisting of hydrogen, alkyl, halo and alkoxy.

4. The method of claim **3** where R' is alkyl.

5. The method of claim **3** where R is an alkyl having 1 to 6 carbon atoms.

6. The method of claim **3** wherein the resin binder of the antihalation composition comprises 9-anthracene ester units.

7. The method of claim **3** wherein the substrate is a microelectronic wafer.

8. The method of claim **3** wherein the substrate is a liquid crystal display substrate.

9. The method of claim **1** where the antihalation composition coating layer further comprises a compound selected from the group consisting of an acid and an acid generator compound.

10. The method of claim **1** where the antihalation composition coating layer further comprises a thermal acid generator.

11. The method of claim **1** where the antihalation composition coating layer comprises a radiation absorbent dye.

12. The method of claim **1** where the crosslinker compound within the antihalation layer is an amine-based material.

13. The method of claim **12** where the crosslinker compound is a melamine resin.

14. The method of claim **12** where the crosslinker is a glycoluril-formaldehyde resin.

15. The method of claim **1** where the photoresist composition is a negative-acting composition.

16. The method of claim **15** wherein the photoresist composition has crosslinked portions after said exposing.

17. The method of claim **1** where the photoresist coating layer is a layer of an acid-hardening photoresist comprising a phenol-based resin binder, an amine-based crosslinker and a photoacid generator.

18. The method of claim **1** wherein the radiation sensitive component of the photoresist composition is a photoacid generator that generates acid upon said exposing.

19. The method of claim **18** wherein the generated acid promotes crosslinking of portions of the photoresist composition layer.

20. The method of claim **1** wherein the photoresist composition is a positive-acting composition.

21. The method of claim **1** wherein the antihalation composition coating layer is at least partially cured prior to applying the photoresist composition coating layer.

22. The method of claim **21** wherein the antihalation composition coating layer is at least partially cured by thermal treatment.

23. The method of claim **21** wherein the antihalation composition coating layer is at least partially cured by exposure of the antihalation composition coating layer to an effective amount of activating radiation.

24. The method of claim **21** further comprising baking the photoresist composition coating layer and antihalation composition coating layer after the exposing and prior to the developing.

25. The method of claim **24** wherein the baking provides crosslinking between the antihalation composition coating layer and the photoresist composition coating layer.

26. The method of claim **1** further comprising baking the photoresist composition coating layer and antihalation composition coating layer after the exposing and prior to the developing.

27. The method of claim **26** wherein the baking provides crosslinking between the antihlation composition coating layer and the photoresist composition coating layer.

28. The method of claim **1** wherein the substrate is a microelectronic wafer.

29. The method of claim **1** wherein the substrate is a liquid crystal display substrate.

* * * * *

United States Patent [19]

Pavelchek et al.

[11] **Patent Number:** **5,939,236**

[45] **Date of Patent:** **Aug. 17, 1999**

[54] **ANTIREFLECTIVE COATING COMPOSITIONS COMPRISING PHOTOACID GENERATORS**

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[51] **Int. Cl.**^{6} **G03F 7/095**

[52] **U.S. Cl.** **430/273.1**; 430/512; 430/926; 430/927

[58] **Field of Search** 430/270.1, 156, 430/512, 926, 927, 273.1

[56] **References Cited**

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4,910,122	3/1990	Arnold et al.	430/313
5,541,037	7/1996	Hatakeyama et al.	430/270.1
5,569,784	10/1996	Watanabe et al.	430/270.1

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0 542 008 A1	5/1993	European Pat. Off. .
WO 90/03598	4/1990	WIPO .
WO 93/22901	11/1993	WIPO .

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[57] **ABSTRACT**

The invention provides new light absorbing crosslinking compositions suitable for use as an antireflective composition, particularly for deep UV applications. The antireflective compositions of the invention comprise a photoacid generator that is activated during exposure of an overcoated photoresist. Antireflective compositions of the invention can significantly reduce undesired footing of an overcoated resist relief image.

29 Claims, No Drawings

ANTIREFLECTIVE COATING COMPOSITIONS COMPRISING PHOTOACID GENERATORS

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to compositions that reduce reflection of exposing radiation from a substrate back into an overcoated photoresist layer. More particularly, the invention relates to antireflective coating compositions that contain a photoacid generator compound that can reduce undesired footing or notching of an overcoated photoresist relief image.

2. Background Art

Photoresists are photosensitive films used for transfer of an image to a substrate. A coating layer of a photoresist is formed on a substrate and the photoresist layer is then exposed through a photomask to a source of activating radiation. The photomask has areas that are opaque to activating radiation and other areas that are transparent to activating radiation. Exposure to activating radiation provides a photoinduced chemical transformation of the photoresist coating to thereby transfer the pattern of the photomask to the photoresist coated substrate. Following exposure, the photoresist is developed to provide a relief image that permits selective processing of a substrate.

A photoresist can be either positive-acting or negative-acting. For most negative-acting photoresists, those coating layer portions that are exposed to activating radiation polymerize or crosslink in a reaction between a photoactive compound and polymerizable reagents of the photoresist composition. Consequently, the exposed coating portions are rendered less soluble in a developer solution than unexposed portions. For a positive-acting photoresist, exposed portions are rendered more soluble in a developer solution while areas not exposed remain comparatively less developer soluble. Photoresist compositions in general are known to the art and described by Deforest, *Photoresist Materials and Processes,* McGraw Hill Book Company, New York, ch. 2, 1975 and by Moreau, *Semiconductor Lithography, Principles, Practices and Materials,* Plenum Press, New York, ch. 2 and 4, both incorporated herein by reference for their teaching of photoresist compositions and methods of making and using the same.

A major use of photoresists is in semiconductor manufacture where an object is to convert a highly polished semiconductor slice, such as silicon or gallium arsenide, into a complex matrix of electron conducting paths, preferably of micron or submicron geometry, that perform circuit functions. Proper photoresist processing is a key to attaining this object. While there is a strong interdependency among the various photoresist processing steps, exposure is believed to be one of the more important steps in attaining high resolution photoresist images.

Reflection of activating radiation used to expose a photoresist often poses limits on resolution of the image patterned in the photoresist layer. Reflection of radiation from the substrate/photoresist interface can produce spatial variations in the radiation intensity in the photoresist, resulting in non-uniform photoresist linewidth upon development. Radiation also can scatter from the substrate/photoresist interface into regions of the photoresist where exposure is not intended, again resulting in linewidth variations. The amount of scattering and reflection will typically vary from region to region, resulting in further linewidth non-uniformity.

Reflection of activating radiation also contributes to what is known in the art as the "standing wave effect". To eliminate the effects of chromatic aberration in exposure equipment lenses, monochromatic or quasi-monochromatic radiation is commonly used in photoresist projection techniques. Due to radiation reflection at the photoresist/substrate interface, however, constructive and destructive interference is particularly significant when monochromatic or quasi-monochromatic radiation is used for photoresist exposure. In such cases the reflected light interferes with the incident light to form standing waves within the photoresist. In the case of highly reflective substrate regions, the problem is exacerbated since large amplitude standing waves create thin layers of underexposed photoresist at the wave minima. The underexposed layers can prevent complete photoresist development causing edge acuity problems in the photoresist profile. The time required to expose the photoresist is generally an increasing function of photoresist thickness because of the increased total amount of radiation required to expose an increased amount of photoresist. However, because of the standing wave effect, the time of exposure also includes a harmonic component which varies between successive maximum and minimum values with the photoresist thickness. If the photoresist thickness is non-uniform, the problem becomes more severe, resulting in variable linewidths.

Variations in substrate topography also give rise to resolution-limiting reflection problems. Any image on a substrate can cause impinging radiation to scatter or reflect in various uncontrolled directions, affecting the uniformity of photoresist development. As substrate topography becomes more complex with efforts to design more complex circuits, the effects of reflected radiation become more critical. For example, metal interconnects used on many microelectronic substrates are particularly problematic due to their topography and regions of high reflectivity.

With recent trends towards high-density semiconductor devices, there is a movement in the industry to shorten the wavelength of exposure sources to deep ultraviolet (DUV) light (300 nm or less in wavelength), KrF excimer laser light (248.4 nm) and ArF excimer laser light (193 nm). The use of shortened wavelengths of light for imaging a photoresist coating has generally resulted in increased reflection from the upper resist surface as well as the surface of the underlying substrate. Thus, the use of the shorter wavelengths has exacerbated the problems of reflection from a substrate surface.

Another approach used to reduce the problem of reflected radiation has been the use of a radiation absorbing layer interposed between the substrate surface and the photoresist coating layer. See, for example, PCT Application WO 90/03598, EPO Application No. 0 639 941 A1 and U.S. Pat. Nos. 4,910,122, 4,370,405 and 4,362,809, all incorporated herein by reference for their teaching of antireflective (antihalation) compositions and the use of the same. Such layers have also been referred to as antireflective layers or antireflective compositions or "ARCs".

In Shipley Company's European Application 542 008 A1 (incorporated herein by reference) highly useful antihalation (antireflective) compositions are disclosed that comprise a resin binder and a crosslinker compound.

While it has been found that prior antireflective compositions may be effective for many antireflective applications, prior compositions also may pose some potential performance limitations, e.g. when the antireflective compositions are used with resist compositions to pattern features of

sub-micron or sub-half micron dimensions. In particular, use of at least some prior antireflective compositions has resulted in undercutting of a developed resist relief image, known in the art as "notching". Another problem has been "footing", i.e. the failure to clear during development that results in an upwardly tapering relief image sidewall. Both notching and footing can compromise the resolution of the image patterned onto the underlying substrate.

It thus would be desirable to have new antireflective coating compositions.

SUMMARY OF THE INVENTION

The present invention provides new light absorbing compositions suitable for use as antireflective coating compositions, particularly for deep UV applications. The antireflective compositions of the invention in general comprise a resin binder and a photoacid generator that can reduce undesired notching and footing of an overcoated photoresist relief image.

It is believed that acids produced by photoacid generators of photoresists, particularly the strong photogenerated acids of chemically-amplified resists, can be highly susceptible to acid neutralization, particularly via base contamination from a substrate or antireflective composition coating layer that underlies a resist layer. Photogenerated acid loss from a resist layer also can occur via diffusion of the acid into an underlying antireflective composition coating layer. In either case of neutralization or diffusion, acid loss can compromise the resolution of the developed resist layer. Typical effects are footing or notching at the base of a resist relief image where the photogenerated acid concentration has been most significantly reduced through such diffusion or neutralization processes.

By incorporating a photoacid generator into the underlying antireflective composition coating layer in accordance with the present invention, sufficient acid can be generated in the antireflective composition layer during exposure of the resist layer to avoid such acid loss from the resist layer and to ensure that an effective amount of acid is present throughout the thickness of the resist layer. In other words, acid diffusion or neutralization from a resist layer can be compensated for by the presence of photogenerated acid in the antireflective composition layer and at the antireflective composition/resist layers interface. As a result, resist relief images having vertical profiles with little or no footing or notching can be produced. See, for instance, the results of the examples and comparative examples which follow.

In the case of crosslinking antireflective compositions of the invention, preferably the antireflective composition photoacid generator is not substantially activated during crosslinking of the antireflective composition. In particular, with respect to antireflective compositions that are thermally crosslinked, the antireflective composition PAG should be substantially stable to the conditions of the crosslinking reaction so that the PAG can be activated and generate acid during subsequent exposure of an overcoated resist layer. Specifically, preferred PAGs do not substantially decompose or otherwise degrade upon exposure of temperatures of from about 140 or 150 to 190° C. for 5 to 30 or more minutes.

For at least some antireflective compositions of the invention, antireflective composition photoacid generators will be preferred that can act as surfactants and congregate near the upper portion of the antireflective composition layer proximate to the antireflective composition/resist coating layers interface. Thus, for example, such preferred PAGs may include extended aliphatic groups, e.g. substituted or

unsubstituted alkyl or alicyclic groups having 4 or more carbons, preferably 6 to 15 or more carbons, or fluorinated groups such as C_{1-15}alkyl or C_{2-15}alkenyl having one or preferably two or more fluoro substituents.

Particularly preferred antireflective composition photoacid generators of the invention can be activated upon exposure to deep UV radiation, particularly about 248 nm and/or about 193 nm, so that the antireflective composition can be effectively used with overcoated deep UV photoresists. Suitably the photoacid generator of the antireflective composition and the photoacid generator of the photoresist composition will be activated at the same exposure wavelength. Sensitizer materials formulated into the photoresist composition and/or antireflective compositions also can be used to ensure that a single exposure wavelength will activate the photoacid generators of both the antireflective and photoresist compositions.

It is further preferred that an antireflective composition of the invention is used together with a photoresist composition where the antireflective composition photoactive compound and photoresist photoactive compound generate the same or approximately the same acid compound (photoproduct) upon exposure to activating radiation during irradiation of the photoresist layer, i.e. photoproducts that preferably have similar diffusion characteristics and similar acid strengths. It has been found that resolution of an overcoated resist relief image is even further enhanced with such matching of the respective antireflective composition and resist photoacid products. References herein to "substantially the same" antireflective composition and resist photoacid products means that those two photoproducts differ no more than no about 2 or 2.5 in pK_a values (measured at 25° C.), preferably the two photoproducts differ no more than about 1 or 1.5 in pK_a values, and still further preferably the two photoproducts differ no more than about 0.75 in pK_a values. It is further preferred that such "substantially the same" antireflective composition and resist photoacid products differ in molecular weight by no more than about 40 percent, preferably by no more than about 20 percent, still more preferably by no more than about 15 percent. It is still further preferred that the antireflective composition and resist photoproducts are each of the same class of acids, e.g. that both photoproducts are sulfonate acids or both are halo-acids such as HBr and the like.

Preferred antireflective compositions of the invention contain a resin binder that contain one or more moieties that are chromophores for the exposure radiation of an overcoated resist composition, i.e. the moieties are capable of absorbing exposure radiation to thereby reduce reflections. For example, for preferred antireflective compositions used with a deep UV (DUV) photoresist, preferred chromophores include anthracenyl, particularly alkylene anthracene esters such as pendant groups of the formula —(C≡O)O(CH₂)ₙanthracene, wherein n is an integer from 1 to about 6. Other preferred chromophores include quinolinyl and ring-substituted quinolinyl derivatives such as hydroxyquinolinyl, phenanthrenyl and acridine groups. Suitably about 5 to 90 percent of the units of a resin comprise such a chromophore, more preferably about 10 to 60 percent. Preferred resin binders of the invention have an optical density of at least about 4 units/μ at the exposure wavelength (e.g. 193 nm or 248 nm). Preferred resin binders also are capable of reaction with the crosslinker component, e.g. by a hydroxy or carboxy moiety on the resin or a "masked" moiety such as an ester that can generate such a reactive group in the presence of acid or otherwise. Preferred antireflective composition resin binders with chromophore moi-

eties are copolymers and are prepared by polymerizing two or more different monomers where at least one of the monomers includes a chromophore group. It has been found that this synthesis provides distinct advantages over functionalization of a preformed polymer to add chromophore groups.

Crosslinking antireflective compositions of the invention preferably also contain an acid or thermal acid generator to induce or promote crosslinking of one or more components of the antireflective composition. Generally preferred crosslinking antireflective compositions comprise a separate crosslinker component such as an amine-based material, e.g. a glycouril, benzoguanamine or melamine resin. Glycouril resins are particularly preferred, especially Powderlink 1174 available from American Cyanamid.

Antireflective compositions of the invention are most preferably used in combination with positive-acting chemically amplified photoresist compositions. Antireflective compositions of the invention are also suitably used with negative-acting photoresists as well as other types of positive resists.

The invention further provides methods for forming a photoresist relief image and novel articles of manufacture comprising substrates coated with an antireflective composition of the invention alone or in combination with a photoresist composition. Other aspects of the invention are disclosed infra.

DETAILED DESCRIPTION OF THE INVENTION

Antireflective compositions of the invention comprise one or more photoacid generators (i.e. "PAG") that are suitably employed in an amount sufficient to inhibit or substantially prevent undesired notching or footing of an overcoated photoresist layer. Suitable amounts of the PAG can vary rather widely and can be readily determined empirically. In general, the one or more PAGs of an antireflective composition of the invention may be suitably employed in amounts of about 0.25 to 5 weight percent or less based on total weight of the antireflective composition. See the examples which follow for exemplary amounts. Particularly preferred amounts of a PAG of an antireflective composition also may vary depending on the characteristics and processing conditions of the photoresist that is used with the antireflective composition. For instance, if the photoresist photoacid generator produces a relatively strong acid photoproduct whereby the photoresist is post-exposure baked (PEB) at relatively low temperatures, then the photoacid product of the antireflective composition will be less likely to thermally decompose at such low PEB temperatures, resulting in a relatively higher effective concentration of acid in the antireflective composition. Accordingly, that antireflective composition can be effectively formulated with a relatively lower concentration of photoacid generator. Conversely, if a photoresist is used that is post-exposure baked at relatively high temperatures, then a portion of the photoacid product of the antireflective composition may be more likely to be thermally decomposed. In such case, the antireflective composition may be formulated with a relatively higher concentration of photoacid generator to ensure an effective concentration of photogenerated acid and maximum reductions of undesired footing.

Sulfonate compounds are preferred PAGs for antireflective compositions of the invention, particularly sulfonate salts. Two specifically preferred agents are the following PAGS 1 and 2:
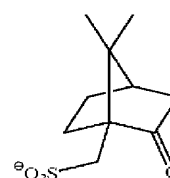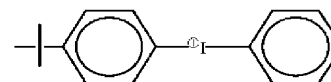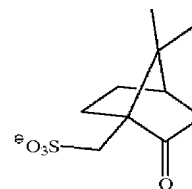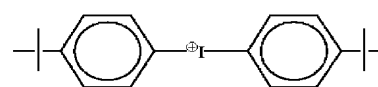
Such sulfonate compounds can be prepared as disclosed in Example 2 which follows, which details the synthesis of above PAG 1. Sulfonate PAG 2 above can be prepared by the same procedures of Example 2 which follows, except approximately molar equivalents of t-butyl benzene and benzene would be reacted together in the first step with acetic anhydride and KIO₃.

Other suitable sulfonate PAGS including sulfonated esters and sulfonyloxy ketones. See *J. of Photopolymer Science and Technology*, 4(3):337–340 (1991), for disclosure of suitable sulfonate PAGS, including benzoin tosylate, t-butylphenyl alpha-(p-toluenesulfonyloxy)-acetate and t-butyl alpha-(p-toluenesulfonyloxy)-acetate. Preferred sulfonate PAGs are also disclosed in U.S. Pat. No. 5,344,742 to Sinta et al.
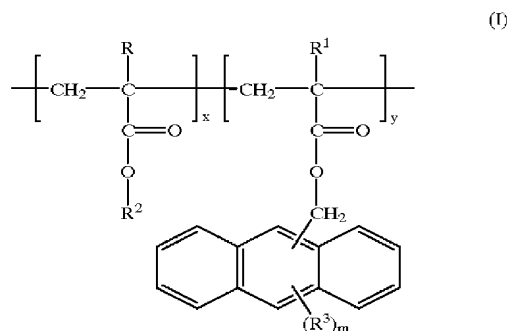
Onium salts also may be employed as photoacid generators of antireflective compositions of the invention. Onium salts that are weakly nucleophilic anions have been found to be particularly suitable. Examples of such anions are the halogen complex anions of divalent to heptavalent metals or non-metals, for example, Sb, Sn, Fe, Bi, Al, Ga, In, Ti, Zr, Sc, D, Cr, Hf, and Cu as well as B, P, and As. Examples of suitable onium salts are diaryl-diazonium salts and onium salts of group Va and B, Ia and B and I of the Periodic Table, for example, halonium salts, quaternary ammonium, phosphonium and arsonium salts, aromatic sulfonium salts and sulfoxonium salts or selenium salts. Examples of suitable preferred onium salts can be found in U.S. Pat. Nos. 4,442, 197; 4,603,101; and 4,624,912.

Other useful acid generators for antireflective compositions of the invention include the family of nitrobenzyl esters, and the s-triazine derivatives. Suitable s-triazine acid generators are disclosed, for example, in U.S. Pat. No. 4,189,323.

Halogenated non-ionic, photoacid generating compounds also may be suitable for antireflective compositions of the invention such as, for example, 1,1-bis[p-chlorophenyl]-2, 2,2-trichloroethane (DDT); 1,1-bis[p-methoxyphenyl]-2,2, 2-trichloroethane; 1,2,5,6,9,10-hexabromocyclodecane; 1,10-dibromodecane; 1,1-bis[p-chlorophenyl]-2,2-

dichloroethane; 4,4-dichloro-2-(trichloromethyl) benzhydrol (Kelthane); hexachlorodimethyl sulfone; 2-chloro-6-(trichloromethyl) pyridine; o,o-diethyl-o-(3,5,6-trichloro-2-pyridyl)phosphorothionate; 1,2,3,4,5,6-hexachlorocyclohexane; N(1,1-bis[p-chlorophenyl]-2,2,2-trichloroethyl)acetamide; tris[2,3-dibromopropyl] isocyanurate; 2,2-bis[p-chlorophenyl]-1,1-dichloroethylene; tris[trichloromethyl]s-triazine; and their isomers, analogs, homologs, and residual compounds. Suitable photoacid generators are also disclosed in European Patent Application Nos. 0164248 and 0232972. Acid generators preferred for deep U.V. exposure include 1,1-bis(p-chlorophenyl)-2,2,2-trichloroethane (DDT); 1,1-bis(p-methoxyphenol)-2,2,2-trichloroethane; 1,1-bis(chlorophenyl)-2,2,2 trichloroethanol; tris(1,2,3-methanesulfonyl)benzene; and tris (trichloromethyl)triazine.

As discussed above, the resin binder component of the antireflective compositions of the invention preferably will effectively absorb reflections in the deep UV range (typically from about 100 to 300 nm). Thus, the resin binder preferably contains units that are deep UV chromophores, i.e. units that absorb deep UV radiation. Highly conjugated moieties are generally suitable chromophores. Aromatic groups, particularly polycyclic hydrocarbon or heterocyclic units, are typically preferred deep UV chromophores, e.g. groups having from two to three or four fused or separate rings with 3 to 8 ring members in each ring and zero to three N, O or S atoms per ring. Such chromophores include substituted and unsubstituted phenanthryl, substituted and unsubstituted anthracyl, substituted and unsubstituted acridine, substituted and unsubstituted naphthyl, substituted and unsubstituted quinolinyl and ring-substituted quinolinyls such as hydroxyquinolinyl groups. Substituted or unsubstituted anthracyl groups are particularly preferred. For example, preferred resin binders have pendant anthracyl groups, particularly acrylic resins of the following Formula (I):

(I)

wherein each R and R^1 is independently a hydrogen or a substituted or unsubstituted alkyl group having from 1 to about 8 carbon atoms, preferably substituted or unsubstituted C$_{1-6}$ alkyl;

each R^2 is independently substituted or unsubstituted alkyl having 1 to about 10 carbon atoms, more typically 1 to about 6 carbons;

each R^3 may be independently halogen (particularly F, Cl and Br), alkyl having 1 to about 8 carbon atoms, alkoxy having 1 to about 8 carbon atoms, alkenyl having 2 to about 8 carbon atoms, alkynyl having 2 to about 8 carbon atoms, cyano, nitro, etc.;

m is an integer of from 0 (where the anthracyl ring is fully hydrogen-substituted) to 9, and preferably m is 0, 1 or 2;

x is the mole fraction or percent of alkyl acrylate units in the polymer and preferably is from about 10 to about 80

percent; and y is the mole fraction or percent of anthracene units in the polymer and preferably is from about 5 to 10 to 90 percent. The polymer also may contain other units if desired, but preferably the polymer will contain at least about 10 mole percent of anthracene units. Hydroxyalkyl is a particularly preferred R^2 group, especially alkyl having a primary hydroxy group such as where R^2 is 2-hydroxyethylene (—CH$_2$CH$_2$OH). Preferably the resin binder contains 9-(methylene)anthracene ester units.

Another preferred resin binder comprises substituted or unsubstituted quinolinyl or a quinolinyl derivative that has one or more N, O or S ring atoms such as a hydroxyquinolinyl. The polymer may contain other units such as carboxy and/or alkyl ester units pendant from the polymer backbone. A particularly preferred antireflective composition resin binder is an acrylic polymer of the following Formula (II):

(II)

wherein each R^4 and R^5 is independently a hydrogen or a substituted or unsubstituted alkyl group having from 1 to about 8 carbon atoms, preferably substituted or unsubstituted C$_{1-6}$ alkyl;

each R^6 is independently substituted or unsubstituted alkyl having 1 to about 10 carbon atoms, more typically 1 to about 6 carbons;

W is a bond or substituted or unsubstituted alkylene having 1 to about 4 carbons, and preferably is a bond;

Z is a carbon, nitrogen, oxygen or sulfur;

each R^7 may be independently halogen (particularly F, Cl and Br), alkyl having 1 to about 8 carbon atoms, alkoxy having 1 to about 8 carbon atoms, alkenyl having 2 to about 8 carbon atoms, alkynyl having 2 to about 8 carbon atoms, cyano, nitro, etc.;

n is an integer of from 0 (where the ring is fully hydrogen-substituted) to 7, and preferably n is 0, 1 or 2.

x' is the mole fraction or percent of alkyl acrylate units in the polymer and preferably is from 10 to about 80 percent; and y' is the mole fraction or percent of quinolinyl or hydroxyquinolinyl units in the polymer and preferably is from about 5 to about 90 percent. The polymer also may contain other units if desired, but preferably the polymer will contain at least about 10 mole percent of quinolinyl and/or hydroxyquinolinyl units. Hydroxyalkyl is a particularly preferred R^6 group, especially alkyl having a primary hydroxy group such as where R^6 is 2-hydroxyethylene.

The above-mentioned substituted groups (including substituted groups R^1 through R^7 and W and substituted PAG substituents) may be substituted at one or more available positions by one or more suitable groups such as e.g. halogen (particularly F, Cl and Br); cyano; hydroxyl, nitro, alkanoyl such as a C$_{1-6}$ alkanoyl group such as acyl and the like; alkyl groups having from 1 to about 8 carbon atoms;

alkenyl and alkynyl groups having one or more unsaturated linkages and 2 to about 8 carbon atoms; alkoxy groups having from 1 to about 6 carbons; etc.

Resin binders for antireflective compositions of the invention are preferably synthesized by polymerizing two or more different monomers where at least one of the monomers includes a chromophore group, e.g. an anthracenyl, quinolinyl or hydroxyquinolinyl group. A free radical polymerization is suitably employed, e.g., by reaction of a plurality of monomers to provide the various units in the presence of a radical initiator preferably under an inert atmosphere (e.g., N_2 or argon) and at elevated temperatures such as about 70° C. or greater, although reaction temperatures may vary depending on the reactivity of the particular reagents employed and the boiling point of the reaction solvent (if a solvent is employed). See Example 1 which follows for exemplary reaction conditions. Suitable reaction temperatures for any particular system can be readily determined empirically by those skilled in the art based on the present disclosure. A reaction solvent may be employed if desired. Suitable solvents include alcohols such as propanols and butanols and aromatic solvents such as benzene, chlorobenzene, toluene and xylene. Dimethylsulfoxide, dimethylformamide and THF are also suitable. The polymerization reaction also may be run neat. A variety of free radical initiators may be employed to prepare the copolymers of the invention. For example, azo compounds may be employed such as azo-bis-2,2'-isobutyronitrile (AIBN) and 1,1'-azobis (cyclohexanecarbonitrile). Peroxides, peresters, peracids and persulfates also can be employed.

Also, while less preferred, a preformed resin may be functionalized with chromophore units. For example, a glycidyl phenolic resin such as a glycidyl novolac can be reacted with an anthranyl carboxylic acid.

Resin binders of antireflective compositions of the invention preferably exhibit good absorbance at deep UV wavelengths such as within the range of from 100 to about 300 nm. More specifically, preferred resin binders of the invention have optical densities of at least about 3 absorbance units per micron (Absorb. units/μ) at the exposing wavelength utilized (e.g. about 248 nm or about 193 nm), preferably from about 5 to 20 or more absorbance units per micron at the exposing wavelength, more preferably from about 4 to 16 or more absorbance units per micron at the exposing wavelength utilized. Higher absorbance values for a particular resin can be obtained by increasing the percentage of chromophore units on the resin.

Preferably resin binders of the above formulae will have a weight average molecular weight (Mw) of about 1,000 to about 10,000,000 daltons, more typically about 5,000 to about 1,000,000 daltons, and a molecular number molecular weight (Mn) of about 500 to about 1,000,000 daltons. Molecular weights (either Mw or Mn) of the polymers of the invention are suitably determined by gel permeation chromatography.
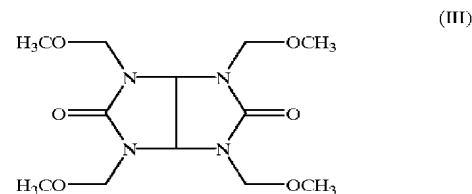
While antireflective composition resin binders having such absorbing chromophores are generally preferred, antireflective compositions of the invention may comprise other resins either as a co-resin or as the sole resin binder component. For example, phenolics, e.g. poly(vinylphenols) and novolaks, may be employed. Such resins are disclosed in the incorporated European Application EP 542008 of the Shipley Company. Other resins described below as photoresist resin binders also could be employed in resin binder components of antireflective compositions of the invention.

The concentration of the resin binder component of the antireflective compositions of the invention may vary within relatively broad ranges, and in general the resin binder is employed in a concentration of from about 50 to 95 weight percent of the total of the dry components of the antireflective composition, more typically from about 60 to 90 weight percent of the total dry components (all components except solvent carrier).

Crosslinking-type antireflective compositions of the invention also contain a crosslinker component. A variety of crosslinkers may be employed, including those antireflective composition crosslinkers disclosed in Shipley European Application 542008 incorporated herein by reference. For example, suitable antireflective composition crosslinkers include amine-based crosslinkers such as a melamine materials, including melamine resins such as manufactured by American Cyanamid and sold under the tradename of Cymel 300, 301, 303, 350, 370, 380, 1116 and 1130. Glycourils are particularly preferred including glycourils available from American Cyanamid. Benzoquanamines and urea-based materials also will be suitable including resins such as the benzoquanamine resins available from American Cyanamid under the name Cymel 1123 and 1125, and urea resins available from American Cyanamid under the names of Beetle 60, 65 and 80. In addition to being commercially available, such amine-based resins may be prepared e.g. by the reaction of acrylamide or methacrylamide copolymers with formaldehyde in an alcohol-containing solution, or alternatively by the copolymerization of N-alkoxymethyl acrylamide or methacrylamide with other suitable monomers.

Low basicity antireflective composition crosslinkers are particularly preferred such as a methoxy methylated glycouril. A specifically preferred crosslinker is a methoxy methylated glycouril corresponding to the following structure (III):

(III)

This methoxy methylated glycouril can be prepared by known procedures. The compound is also commercially available under the tradename of Powderlink 1174 from the American Cyanamid Co.

Other suitable low basicity crosslinkers include hydroxy compounds, particularly polyfunctional compounds such as phenyl or other aromatics having one or more hydroxy or hydroxy alkyl substituents such as a C_{1-8} hydroxyalkyl substituents. Phenol compounds are generally preferred such as di-methanolphenol ($C_6H_3(CH_2OH)_2OH$) and other compounds having adjacent (within 1–2 ring atoms) hydroxy and hydroxyalkyl substitution, particularly phenyl or other aromatic compounds having one or more methanol or other hydroxylalkyl ring substituent and at least one hydroxy adjacent such hydroxyalkyl substituent.

It has been found that a low basicity crosslinker such as a methoxy methylated glycouril used in antireflective compositions of the invention can provide excellent lithographic performance properties, including significant reduction (SEM examination) of undercutting or footing of an overcoated photoresist relief image.

A crosslinker component of antireflective compositions of the invention in general is present in an amount of between

5,939,236

11   12

5 and 50 weight percent of total solids (all components except solvent carrier) of the antireflective composition, more typically in an amount of about 7 to 25 weight percent total solids.

Crosslinking antireflective compositions of the invention preferably further comprise an acid or thermal acid generator compound for catalyzing or promoting crosslinking during curing of an antireflective composition coating layer. Preferably a thermal acid generator is employed, i.e. a compound that generates acid upon thermal treatment. A variety of known thermal acid generators are suitably employed such as e.g. 2,4,4,6-tetrabromocyclohexadienone, benzoin tosylate, 2-nitrobenzyl tosylate and other alkyl esters of organic sulfonic acids. Compounds that generate a sulfonic acid upon activation are generally suitable. Typically a thermal acid generator is present in an antireflective composition in concentration of from about 0.1 to 10 percent by weight of the total of the dry components of the composition, more preferably about 2 percent by weight of the total dry components.

Also, as discussed above, rather than a thermal acid generator, an acid may be simply formulated into the antireflective composition, particularly for antireflective compositions that require heating to cure in the presence of acid so that the acid does not promote undesired reaction of composition components prior to use of the antireflective composition. Suitable acids include e.g. strong acids such as sulfonic acids such as toluene sulfonic acid and sulfonic acid, triflic acid, or mixtures of those materials.

The present invention also includes antireflective compositions that do not undergo significant cross-linking during intended use with a photoresist composition. Such non-crosslinking antireflective compositions include a photoacid generator as disclosed herein, but need not include a crosslinker component or an acid or thermal acid generator for inducing or promoting a crosslinking reaction. In other words, such non-crosslinking antireflective compositions typically will be essentially free (i.e. less than about 1 or 2 weight percent) or completely free of a crosslinker component and/or a thermal acid generator.

Antireflective compositions of the invention also may contain additional dye compounds that absorb radiation used to expose an overcoated photoresist layer. Other optional additives include surface leveling agents, for example, the leveling agent available under the tradename Silwet 7604 from Union Carbide, or the surfactant FC 171 or FC 431 available from the 3M Company.

To make a liquid coating composition, the components of the antireflective composition are dissolved in a suitable solvent such as, for example, ethyl lactate or one or more of the glycol ethers such as 2-methoxyethyl ether (diglyme), ethylene glycol monomethyl ether, and propylene glycol monomethyl ether; solvents that have both ether and hydroxy moieties such as methoxy butanol, ethoxy butanol, methoxy propanol and ethoxy propanol; esters such as methyl cellosolve acetate, ethyl cellosolve acetate, propylene glycol monomethyl ether acetate, dipropylene glycol monomethyl ether acetate and other solvents such as dibasic esters, propylene carbonate and gamma-butyro lactone. The concentration of the dry components in the solvent will depend on several factors such as the method of application. In general, the solids content of an antireflective composition varies from about 0.5 to 20 weight percent of the total weight of the antireflective composition, preferably the solids content varies from about 2 to 10 weight percent of the total weight of the antireflective composition.

A variety of photoresist compositions can be employed with the antireflective compositions of the invention, including positive-acting and negative-acting photoacid-generating compositions. Photoresists used with antireflective compositions of the invention typically comprise a resin binder and a photoactive component, typically a photoacid generator compound. Preferably the photoresist resin binder has functional groups that impart alkaline aqueous developability to the imaged resist composition.

As discussed above, particularly preferred photoresists for use with antireflective compositions of the invention are chemically-amplified resists, particularly positive-acting chemically-amplified resists compositions, where the photoactivated acid in the resist layer induces a deprotection-type reaction of one or more composition components to thereby provide solubility differentials between exposed and unexposed regions of the resist coating layer.

A number of chemically-amplified resist compositions have been described, e.g., in U.S. Pat. Nos. 4,968,581; 4,883,740; 4,810,613; 4,491,628 and 5,492,793, all of which are incorporated herein by reference for their teaching of making and using chemically amplified positive-acting resists. A particularly preferred chemically amplified photoresist for use with an antireflective composition of the invention comprises in admixture a photoacid generator and a resin binder that comprises a copolymer containing both phenolic and non-phenolic units. For example, one preferred group of such copolymers has acid labile groups substantially, essentially or completely only on non-phenolic units of the copolymer. One especially preferred copolymer binder has repeating units x and y of the following formula:

wherein the hydroxyl group be present at either the ortho, meta or para positions throughout the copolymer, and R' is substituted or unsubstituted alkyl having 1 to about 18 carbon atoms, more typically 1 to about 6 to 8 carbon atoms. Tert-butyl is a generally preferred R' group. An R' group may be optionally substituted by e.g. one or more halogen (particularly F, Cl or Br), C_{1-8} alkoxy, C_{2-8} alkenyl, etc. The units x and y may be regularly alternating in the copolymer, or may be randomly interspersed through the polymer. Such copolymers can be readily formed. For example, for resins of the above formula, vinyl phenols and a substituted or unsubstituted alkyl acrylate such as t-butylacrylate and the like may be condensed under free radical conditions as known in the art. The substituted ester moiety, i.e. R'—O—C(=O)—, moiety of the acrylate units serves as the acid labile groups of the resin and will undergo photoacid induced cleavage upon exposure of a coating layer of a photoresist containing the resin. Preferably the copolymer will have a Mw of from about 8,000 to about 50,000, more preferably about 15,000 to about 30,000 with a molecular weight distribution of about 3 or less, more preferably a molecular weight distribution of about 2 or less. Non-phenolic resins, e.g. a copolymer of an alkyl acrylate such as t-butylacrylate or t-butylmethacrylate and a vinyl alicyclic such as a vinyl norbornyl or vinyl cyclohexanol compound, also may be used as a resin binder in compositions of the invention. Such copolymers also may be prepared by such

free radical polymerization or other known procedures and suitably will have a Mw of from about 8,000 to about 50,000, and a molecular weight distribution of about 3 or less. Additional preferred chemically-amplified positive resists are disclosed in U.S. Pat. No. 5,258,257 to Sinta et al.

The antireflective compositions of the invention also may be used with other positive resists, including those that contain resin binders that comprise polar functional groups such as hydroxyl or carboxylate and the resin binder is used in a resist composition in an amount sufficient to render the resist developable with an aqueous alkaline solution. Generally preferred resist resin binders are phenolic resins including phenol aldehyde condensates known in the art as novolak resins, homo and copolymers or alkenyl phenols and homo and copolymers of N-hydroxyphenyl-maleimides.

Copolymers containing phenol and nonaromatic cyclic alcohol units also are preferred resin binders for resists of the invention and may be suitably prepared by partial hydrogenation of a novolak or poly(vinylphenol) resin. Such copolymers and the use thereof in photoresist compositions are disclosed in U.S. Pat. No. 5,128,232 to Thackeray et al.

Preferred negative-acting resist compositions for use with an antireflective composition of the invention comprise a mixture of materials that will cure, crosslink or harden upon exposure to acid, and a photoacid generator.

Particularly preferred negative-acting resist compositions comprise a resin binder such as a phenolic resin, a crosslinker component and a photoactive component of the invention. Such compositions and the use thereof have been disclosed in European Patent Applications 0164248 and 0232972 and in U.S. Pat. No. 5,128,232 to Thackeray et al. Preferred phenolic resins for use as the resin binder component include novolaks and poly(vinylphenol)s such as those discussed above. Preferred crosslinkers include amine-based materials, including melamine, glycourils, benzoguanamine-based materials and urea-based materials. Melamine-formaldehyde resins are generally most preferred. Such crosslinkers are commercially available, e.g. the melamine resins sold by American Cyanamid under the trade names Cymel 300, 301 and 303. Glycouril resins are sold by American Cyanamid under trade names Cymel 1170, 1171, 1172, Powderlink 1174, urea-based resins are sold under the trade names of Beetle 60, 65 and 80, and ben zoguanamine resins are sold under the trade names Cymel 1123 and 1125.

Suitable photoacid generator compounds of resists used with antireflective compositions of the invention include the onium salts, such as those disclosed in U.S. Pat. Nos. 4,442,197, 4,603,101, and 4,624,912, each incorporated herein by reference; and non-ionic organic photoactive compounds such as the halogenated photoactive compounds as in U.S. Pat. No. 5,128,232 to Thackeray et al. and sulfonate photoacid generators including sulfonated esters and sulfonyloxy ketones. See *J. of Photopolymer Science and Technology*, 4(3):337–340 (1991), for disclosure of suitable sulfonate PAGS, including benzoin tosylate, t-butylphenyl alpha-(p-toluenesulfonyloxy)-acetate and t-butyl alpha-(p-toluenesulfonyloxy)-acetate. Preferred sulfonate PAGs are also disclosed in U.S. Pat. No. 5,344,742 to Sinta et al. The above camphorsulfonate PAGs 1 and 2 are also preferred photoacid generators for resist compositions used with the antireflective compositions of the invention, particularly chemically-amplified resists of the invention.

Photoresists for use with an antireflective composition of the invention also may contain other materials. For example, other optional additives include actinic and contrast dyes,

anti-striation agents, plasticizers, speed enhancers, etc. Such optional additives typically will be present in minor concentration in a photoresist composition except for fillers and dyes which may be present in relatively large concentrations such as, e.g., in amounts of from 5 to 30 percent by weight of the total weight of a resist's dry components.

Antireflective compositions of the invention that include a low basicity crosslinker such as a suitable glycouril are particularly useful with photoresists that generate a strong acid photoproduct upon exposure such as triflic acid, camphor sulfonate or other sulfonic acid, or other acid having a pKa (25° C.) of about 2 or less. Without wishing to be bound by theory, it is believed that antireflective compositions of the invention are particularly effective with such strong acid resists because the strong photogenerated acid will migrate from the resist and remain in the antireflective composition layer to a lesser extent relative to a comparable antireflective composition that contains a more basic crosslinker. That is, the low basicity crosslinkers of the invention will tie up strong photogenerated acids of an overcoated resist layer to a lesser extent than a more basic antireflective composition crosslinker. As a result, less acid loss from the resist layer will occur and resolution problems such as footing will be even further reduced.

In use, an antireflective composition of the invention is applied as a coating layer to a substrate may any of a variety of methods such as spin coating. The antireflective composition in general is applied on a substrate with a dried layer thickness of between about 0.02 and 0.5 μm, preferably a dried layer thickness of between about 0.04 and 0.20 μm. The substrate is suitably any substrate used in processes involving photoresists. For example, the substrate can be silicon, silicon dioxide or aluminum-aluminum oxide microelectronic wafers. Gallium arsenide, ceramic, quartz or copper substrates may also be employed. Substrates used for liquid crystal display or other flat panel display applications are also suitably employed, for example glass substrates, indium tin oxide coated substrates and the like. Substrates for optical and optical-electronic devices (e.g. waveguides) also can employed.

Preferably the antireflective layer is cured before a photoresist composition is applied over the antireflective composition. Cure conditions will vary with the components of the antireflective composition. Thus, if the composition does not contain an acid or thermal acid generator, cure temperatures and conditions will be more vigorous than those of a composition containing an acid or acid generator compound. Typical cure conditions are from about 120° C. to 225° C. for about 0.5 to 40 minutes. Cure conditions preferably render the antireflective composition coating layer substantially insoluble to the photoresist solvent as well as an alkaline aqueous developer solution.

After such curing a photoresist is applied over the surface of the antireflective composition. As with application of the antireflective composition, the photoresist can be applied by any standard means such as by spinning, dipping, meniscus or roller coating. Following application, the photoresist coating layer is typically dried by heating to remove solvent preferably until the resist layer is tack free. Optimally, essentially no intermixing of the antireflective composition layer and photoresist layer should occur.

The resist layer is then imaged with activating radiation through a mask in conventional manner. The exposure energy is sufficient to effectively activate the photoactive component of the resist system to produce a patterned image in the resist coating layer as well as activate the photoacid

generator of at least a portion of the thickness of antireflective composition layer so that photogenerated acid from the PAG of the antireflective composition is present at the antireflective composition/resist coating layers interface. Typically, the exposure energy typically ranges from about 3 to 300 mJ/cm² and depending in part upon the exposure tool and the particular resist and resist processing that is employed. Generally, exposure doses used for typical imaging of a resist layer will be sufficient to photoactivate an effective of acid in the underlying antireflective composition layer.

The exposed resist layer may be subjected to a post-exposure bake if desired to create or enhance solubility differences between exposed and unexposed regions of a coating layer. For example, negative acid-hardening photoresists typically require post-exposure heating to induce the acid-promoted crosslinking reaction, and many chemically amplified positive-acting resists require post-exposure heating to induce an acid-promoted deprotection reaction. Typically post-exposure bake conditions include temperatures of about 50° C. or greater, more specifically a temperature in the range of from about 50° C. to 160° C.

The exposed resist coating layer is then developed, preferably with an aqueous based developer such as an inorganic alkali exemplified by tetrabutyl ammonium hydroxide, sodium hydroxide, potassium hydroxide, sodium carbonate, sodium bicarbonate, sodium silicate, sodium metasilicate, aqueous ammonia or the like. Alternatively, organic developers can be used. In general, development is in accordance with art recognized procedures. Following development, a final bake of an acid-hardening photoresist is often employed at temperatures of from about 100 to 150° C. for several minutes to further cure the developed exposed coating layer areas.

The developed substrate may then be selectively processed on those substrates areas bared of photoresist, for example chemically etching or plating substrate areas bared of photoresist in accordance with procedures well known in the art. Suitable etchants include a hydrofluoric acid etching solution and a plasma gas etch such as an oxygen plasma etch. A plasma gas etch removes the crosslinked antihalation coating layer.

All documents mentioned herein are incorporated herein by reference. The following non-limiting examples are illustrative of the invention.

EXAMPLE 1

Preparation of Preferred Antireflective Composition Resin Binders

Hydroxyethyl methacrylate (HEMA)/methylanthracene methacrylate (ANTMA) copolymer (Formula 1 above) was prepared as follows.

A 300 ml 3N round bottom flask equipped with magnetic stirrer, condenser, nitrogen and vacuum inlet was charged with 16.0 g (0.1229 mol) HEMA (purified by distillation), 8.49 g (0.0307 mol) methylanthracene methacrylate, 0.2449 g (1 wt. %) AIBN and 180 ml THF. The reaction flask was quenched in liquid nitrogen while being purged with nitrogen. When the contents of the reaction flask were frozen, the flask was evacuated, then purged with nitrogen (3 times). The reaction mixture was stirred under reflux for 18 hours. The pale yellow polymer was precipitated into 3000 ml ether, filtered, then dried at 50° C. under vacuum (yield 86%) to provide the HEMA/ANTMA copolymer having 81 mole percent of —CH₂C(CH₃)(CO₂CH₂CH₂OH)— units

and 19 mole percent of —CH₂C(CH₃)(CO₂CH₂-9-anthracene) units, a Mn of 2295, Mw of 19150 and a Tg of 101° C.

EXAMPLE 2

Preparation of di(4-t-butylphenyl)iodonium(+/−)-10-camphor sulfonate

The PAG 1 above can be prepared as follows. A 2 L 3 neck round bottom flask was charged with potassium iodate (214.00 g, 1.00 mol), t-butylbenzene (268.44 g, 2.00 mol) and acetic anhydride (408.36 g, 4.00 mol). The flask was fitted with an efficient overhead paddle stirrer, a thermometer and a pressure equalizing dropping funnel fitted with a N₂ bubbler. The reaction mixture was cooled to 10° C. in a ice-water bath and concentrated sulfuric acid (215.78 g, 2.20 mol) added dropwise via the addition funnel. The addition was carried out at such a rate as to maintain the reaction temperature around 25° C. and required 2 hours. As the addition proceeded the starting white suspension became orange-yellow in color. Once the addition was over, the reaction mixture was stirred at room temperature (20° C.) for an additional 22 hours. The reaction mixture was cooled to 5–10° C. and water (600 ml) was added dropwise over a period of 30 minutes, maintaining the temperature below 30° C. (Note the first @75 ml should be added at a particular slow rate as to control the initial exotherm, thereafter the rest of the water may be added at a faster rate). This cloudy mixture was washed with hexane (3×100 ml) (to remove unreacted t-butylbenzene and some 4-t-butyliodobenzene byproduct) in a 2 L separating funnel and the aqueous solution of diaryliodonium hydrogensulfate transferred to a 3 L reaction vessel. The solution was cooled to 5–10° C., (+/−)-10-camphorsulfonic acid (232.30 g, 1.00 mol) was added in one portion with stirring and the solution was then neutralized with ammonium hydroxide (620 ml, 9.20 mol). The amount of base used was the theoretical amount required to neutralize all acidic species in the pot, assuming quantitative reaction. The addition of the base is carried out at such a rate as to keep the temperature below 25° C. and takes about 1 hour. As the addition nears completion and the pH of the reaction mixture approaches 7, the crude diaryliodonium camphorsulfonate precipitated as a tan solid. This suspension was allowed to stir at room temperature for 3 hours and the material isolated as follows: The tan solid was collected by suction filtration and while still moist taken up in dichloromethane (1 L) and washed with dilute ammonium hydroxide (2.5 wt %, 5 ml 14.8 N NH₄OH+195 ml H₂O) until the washings are in the pH 7–8 range (1×200 ml) and then water (2×200 ml) to restore the pH to around 7. After drying (MgSO₄), the dichloromethane was removed under reduced pressure and the residue further dried in vacuo at 50° C. for 16 hours to give the crude product as a tan solid (390.56 g). The resulting tan solid was then purified by recrystallization in the following manner. The tan solid was dissolved in the minimum amount of refluxing isopropanol (@ 375 g PAG in @ 1150 ml IPA) in a 2 L round bottom flask to give a homogeneous dark red solution. The hot solution was transferred to a 2 L conical flask and allowed to cool. While this solution was still warm, hexane (500 ml) was added and crystals formed soon after. The crystallizing mixture was allowed to cool to room temperature and stored for 4 hours. The crystallizing solution was cooled to @ 5° C. in an ice-water bath for 1.5 hours and then the solid was collected by suction filtration and washed until white with very cold isopropanol-hexane (1:3, 2×200 ml, prepared by cooling the solvent mixture in a dry ice-acetone bath before

use). The white solid was dried under aspirator vacuum for 1 hour until the PAG (di-(4-t-butylphenyl)iodonium (+/−)-10-camphor sulfonate) was isolated as a free flowing white powder. At this stage about 285 g of PAG is obtained. A second recrystallization can be performed in a similar manner.

Examples 3–4 and Comparative Examples 1A-B and 2
Preparation and Use of Antireflective Compositions of the Invention and Comparative Examples

EXAMPLE 3

A preferred antireflective composition of the invention was prepared by mixing the components set forth below, with component amounts expressed as parts by weight based on total weight of the liquid antireflective coating composition:

1) Resin binder: 2.17% Polymer (novolac resin base with approximately 4% glycidyl groups replacing OH, and approximately 80% of OH groups replaced by —O(C=O)CH₂9-anthracene)

2) Crosslinker: 0.61% Powderlink 1174 (American Cyanamid)

3) Acid: 0.06% p-toluene sulfonic acid

4) Photoacid generator: 0.16% di-t-butyl diphenyl iodonium camphorsulfonate

5) Surfactant: 0.03% FC 171 (3M Co.)

6) Solvent: 18% ethyl lactate; 10% cyclohexanone; and 68.97% propylene glycol monomethyl ether

The antireflective composition was spin coated onto a single crystal silicon substrate 100 mm in diameter, and baked on a vacuum hot plate at 175° C. for 60 seconds. The resulting thickness was 600 angstroms. Over this antireflective composition layer a commercially available DUV positive photoresist (sold under the tradename of UVIIHS and available from the Shipley Company) was applied to a thickness of 7950 Å after a vacuum hot plate bake at 135° C. for 60 seconds. The overcoated resist layer was exposed to KrF excimer radiation (248 nm) with an ISI XLS projection stepper through a mask patterned with small lines and spaces with a dose of 12.0 mJ/cm². The wafer was then baked on a vacuum hot plate at 130° C. for 90 seconds, and then developed with CD-26 developer (Shipley Co.; alkaline aqueous solution) for 60 seconds. Resist footing was measured by cross-section SEMs (scanning electron micrographs) for both isolated and dense lines 0.25 μm wide and averaged 3 nm.

COMPARATIVE EXAMPLE 1A

The same antireflective composition was prepared as described above in Example 3, except the photoacid generator was omitted. This antireflective composition was spin coated onto a single crystal silicon substrate 100 mm in diameter, and baked on a vacuum hot plate at 205° C. for 60 seconds. The resulting thickness was 600 angstroms. Over this antireflective composition layer a commercially available DUV positive photoresist (sold under the tradename of UVIIHS and available from the Shipley Company) was applied to a thickness of 7950 Å after a vacuum hot plate bake at 135° C. for 60 seconds. The overcoated resist layer was exposed to KrF excimer radiation (248 nm) with an ISI XLS projection stepper through a mask patterned with small lines and spaces with a dose of 10.5 mJ/cm². The wafer was then baked on a vacuum hot plate at 130° C. for 60 seconds, and then developed with CD-26 developer (Shipley Co.; alkaline aqueous solution) for 60 seconds. Resist footing

was measured by cross-section SEMs for both isolated and dense lines 0.25 μm wide and averaged 39 nm.

COMPARATIVE EXAMPLE 1B

The same antireflective composition was prepared as described above in Example 3, except N-(perfluoro-1-octanesulfonyloxy)-5-norbornene-2,3-dicarboximide was substituted for the diphenyl iodonium camphorsulfonate PAG of Example 3. N-(perfluoro-1-octanesulfonyloxy)-5-norbornene-2,3-dicarboximide is less thermally stable than diphenyl iodonium camphorsulfonate and can undergo decomposition at about 150° C. This antireflective composition was spin coated onto a single crystal silicon substrate 100 mm in diameter, and baked on a vacuum hot plate at 175° C. for 60 seconds. The resulting thickness was 600 angstroms. Over this antireflective composition layer a commercially available DUV positive photoresist (sold under the tradename of UVIIHS and available from the Shipley Company) was applied to a thickness of 7950 Å after a vacuum hot plate bake at 130° C. for 60 seconds. The overcoated resist layer was exposed to KrF excimer radiation (248 nm) with an ISI XLS projection stepper through a mask patterned with small lines and spaces with a dose of 12.0 mJ/cm². The wafer was then baked on a vacuum hot plate at 135° C. for 90 seconds, and then developed with CD-26 developer (Shipley Co.; alkaline aqueous solution) for 60 seconds. Resist footing was measured by cross-section SEMs for both isolated and dense lines 0.25 μm wide and averaged 17 nm.

EXAMPLE 4

A further preferred antireflective composition of the invention was prepared by mixing the components set forth below, with component amounts expressed as parts by weight based on total weight of the liquid antireflective coating composition:

1) Resin binder: 2.48% copolymer of 9-anthrylmethylmethacrylate (26mol%) and 2-hydroxyethylmethacrylate (74 mol%)

2) Crosslinker: 0.36% Powderlink 1174 (American Cyanamid)

3) Acid: 0.04% p-nitrobenzyl tosylate

4) Photoacid generator: 0.04% di-t-butyl diphenyl iodonium camphorsulfonate

5) Surfactant: 0.03% FC 431 (3M Co.)

6) Solvent: 97.05% propylene glycol monomethyl ether

The antireflective composition was spin coated onto a single crystal silicon substrate 100 mm in diameter, and baked on a vacuum hot plate at 175° C. for 60 seconds. The resulting thickness was 605 angstroms. Over this antireflective composition layer a commercially available DUV positive photoresist (sold under the tradename of UVIIHS and available from the Shipley Company) was applied to a thickness of 8620 Å after a vacuum hot plate bake at 135° C. for 60 seconds. The overcoated resist layer was exposed to KrF excimer radiation (248 nm) with an ISI XLS projection stepper through a mask patterned with small lines and spaces with a dose of 11.0 mJ/cm². The wafer was then baked on a vacuum hot plate at 130° C. for 90 seconds, and then developed with CD-26 developer (Shipley Co.; alkaline aqueous solution) for 60 seconds. Resist footing was measured by cross-section SEMs for both isolated and dense lines 0.25 μm wide and averaged approximately 12 nm.

COMPARATIVE EXAMPLE 2

The same formulation was prepared as described above in Example 4, except the photoacid generator was omitted.

This formulation was spin coated onto a single crystal silicon substrate 100 mm in diameter, and baked on a vacuum hot plate at 175° C. for 60 seconds. The resulting thickness was 600 angstroms. Over this antireflective composition layer a commercially available DUV positive photoresist (sold under the tradename of UVIIHS and available from the Shipley Company) was applied to a thickness of 7950 Å after a vacuum hot plate bake at 135° C. for 60 seconds. The overcoated resist layer was exposed to KrF excimer radiation (248 nm) with an ISI XLS projection stepper through a mask patterned with small lines and spaces with a dose of 10.8 mJ/cm². The wafer was then baked on a vacuum hot plate at 130° C. for 60 seconds, and then developed with CD-26 developer (Shipley Co.; alkaline aqueous solution) for 60 seconds. Resist footing was measured by cross-section SEMs for both isolated and dense lines 0.25 μm wide and averaged 27 nm.

The foregoing description of the invention is merely illustrative thereof, and it is understood that variations and modifications can be effected without departing from the scope or spirit of the invention as set forth in the following claims.

What is claimed is:

1. A coated substrate comprising:

a substrate having thereon
   1) a coating layer of an antireflective composition that comprises a) a resin binder, b) an acid or thermal acid generator, and c) a photoacid generator compound; and
   2) a coating layer of a photoresist over the antireflective composition coating layer, the photoresist comprising a resin and a photoacid generator compound.

2. The coated substrate of claim 1 wherein the photoresist is a chemically-amplified positive-acting photoresist that comprises a resin binder and a photoacid generator compound.

3. The coated substrate of claim 1 wherein the antireflective composition photoacid generator compound and the photoresist photoacid generator compound each generate substantially the same acid compound upon exposure to activating radiation.

4. The coated substrate of claim 1 wherein the antireflective composition photoacid generator compound and the photoresist photoacid generator compound each generate the same acid compound upon exposure to activating radiation.

5. The coated substrate of claim 4 wherein the antireflective composition photoacid generator compound and the photoresist photoacid generator compound each generate a sulfonate acid upon exposure to activating radiation.

6. The coated substrate of claim 1 wherein the substrate is a microelectronic wafer, a flat panel display substrate or an optical-electronic substrate.

7. The coated substrate of claim 1 wherein the photoacid generator of the antireflective composition is substantially stable upon exposure to temperatures of from about 110 to 175° C. for at least about 1 minute.

8. The coated substrate of claim 1 wherein the photoacid generator of the antireflective composition generates acid upon exposure to an effective amount of radiation having a wavelength of about 248 nm or 193 nm.

9. The coated substrate of claim 1 wherein the photoacid generator of the antireflective composition has one or more substituted or unsubstituted alkyl or substituted or unsubstituted alicyclic groups having 4 or more carbons.

10. The coated substrate of claim 3 wherein the antireflective composition photoacid generator compound and the photoresist photoacid generator compound generate upon exposure to activating radiation photoacid products that differ about 1.5 or less in pka values.

11. The coated substrate of claim 3 wherein the antireflective composition photoacid generator compound and the photoresist photoacid generator compound generate upon exposure to activating radiation photoacid products that differ in molecular weight by about 20 percent or less.

12. The coated substrate of claim 4 wherein the antireflective composition photoacid generator compound and the photoresist photoacid generator compound each generated a halo-acid upon each to activating radiation.

13. The coated substrate of claim 1 wherein the antireflective composition resin binder comprises anthracenyl units.

14. The coated substrate of claim 1 wherein the antireflective composition resin binder comprises quinolinyl, hydroxyquinolinyl, phenanthrenyl or acridine groups.

15. The coated substrate of claim 1 wherien the antireflective composition comprises a crosslinker.

16. The coated substrate of claim 15 wherein the crosslinker is an amine-based material.

17. The coated substrate of claim 16 wherein the crosslinker is a glycouril resin.

18. A coated substrate comprising:

a substrate having thereon
   1) a coating layer of an antireflective composition comprising a resin binder, and a photoacid generator, the antireflective composition at least essentially free of a crosslinker component; and
   2) a coating layer of a chemically-amplified positive-acting photoresist over the antireflective composition coating layer, the photoresist comprising a resin and a photoacid generator compound.

19. The coated substrate of claim 18 wherein the photoacid generator of the antireflective composition is substantially stable upon exposure to temperatures of from about 110 to 175° C. for at least about 1 minute.

20. The coated substrate of claim 18 wherein the photoacid generator of the antireflective composition generates acid upon exposure to an effective amount of radiation having a wavelength of about 248 nm or 193 nm.

21. The coated substrate of claim 18 wherein the photoacid generator of the antireflective composition has one or more substitited or unsubstituted alkyl or alicyclic groups having 4 or more carbons.

22. The coated substrate of claim 18 wherein the antireflective composition photoacid generator compound and the photoresist photoacid generator compound generate upon exposure to activating radiation photoacid products that differ about 1.5 or less in pka values.

23. The coated substrate of claim 18 wherein the antireflective composition photoacid generator compound and the photoresist photoacid generator compound generate upon exposure to activating radiation photoacid products that differ in molecular weight by about 20 percent or less.

24. The coated substrate of claim 18 wherein the antireflective composition photoacid generator compound and the photoresist photoacid generator compound each generate substantially the same acid compound upon exposure to activating radiation.

25. The coated substrate of claim 18 wherein the antireflective composition photoacid generator compound and the photoresist photoacid generator compound each generate the same acid compound upon exposure to activating radiation.

26. The coated substrate of claim **18** wherein the antireflective composition photoacid generator compound and the photoresist photoacid generator compound each generate a halo-acid upon exposure to activating radiation.

27. The coated substrate of claim **18** wherein the antireflective composition photoacid generator compound and the photoresist photoacid generator compound each generate a sulfonate acid upon exposure to activating radiation.

28. The coated substrate of claim **18** wherein the antireflective composition resin binder comprises anthracenyl units.

29. The coated substrate of claim **18** wherein the antireflective composition resin binder comprises quinolinyl, hydroxyquinolinyl, phenanthrenyl or acridine groups.

* * * * *

(12) **United States Patent** (10) Patent No.: **US 6,277,750 B1**

Pawlowski et al. (45) Date of Patent: **Aug. 21, 2001**

(54) **COMPOSITION FOR BOTTOM REFLECTION PREVENTIVE FILM AND NOVEL POLYMERIC DYE FOR USE IN THE SAME**

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(58) **Field of Search** 438/636, 689, 438/707, 708, 710, 725; 216/41, 49, 50; 430/313, 314, 323, 332

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(57) **ABSTRACT**

As a bottom anti-reflective coating material for use in photolithography, polymer dyes represented by following general formula are used. The polymer dyes are able to form a bottom anti-reflective coating having good film formation properties, good absorption properties at exposure wavelength, good step coverage, non-intermixing with photoresist and high etch rate.
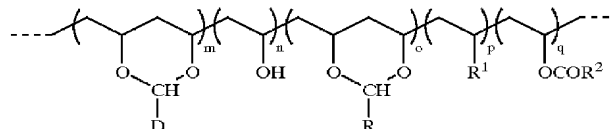
wherein

R represents H or a substituted or non-substituted alkyl, cycloalkyl, or aryl group, R^1 represents a substituted or non-substituted alkyl or aryl, or a —$COOR^3$ group in which R^3 represents an alkyl group, R^2 represents a substituted or non-substituted alkyl, cycloalkyl, or aryl group, D is an organic chromophore which absorbs at the exposure wavelength (150–450 nm) and represents a substituted or non-substituted aryl, condensed aryl, or heteroaryl group, m and o are any integer above zero, and n, p and q are any integer including zero.

18 Claims, No Drawings

COMPOSITION FOR BOTTOM REFLECTION PREVENTIVE FILM AND NOVEL POLYMERIC DYE FOR USE IN THE SAME

TECHNICAL FIELD

This invention relates to a novel composition for a bottom anti-reflective coating composition, a method of forming a bottom anti-reflective coating between a substrate and a photoresist layer using the bottom anti-reflective coating composition and manufacturing integrated circuits utilizing a photolithography method, and novel polymer dyes. More particularly this invention relates to a composition for a bottom anti-reflective coating comprising at least a solvent and a novel polymer dye having recurrent cyclic acetal units, and a method of forming a bottom anti-reflective coating by using the composition and manufacturing integrated circuits by utilizing a photolithography method, novel polymer dyes, and a method of producing thereof.

BACKGROUND ART

In manufacturing integrated circuits and active elements and interconnecting structures within microelectronic devices, a photolithography technique using photoresist compositions is utilized. In general the manufacturing of the integrated circuits or microelectronic devices are conducted as followed. That is, first, a photoresist material dissolved in a solvent is applied on a substrate such as silicon wafer by spin coating. The substrate coated with resist is then baked at elevated temperatures to evaporate any solvent in the photoresist composition and to form a thin photoresist layer with good adhesion to the substrate. The thin photoresist layer on the wafer was subjected to an imagewise exposure to radiation in the range of 150 to 450 nm wavelength, such as visible or ultraviolet (UV) rays. The imagewise exposure may also be conducted by electron beam or X-ray radiation in place of such visible or UV rays. In the exposed areas of the photoresist layer the chemical transformation arises by the exposure. After the imagewise exposure, the substrate with an imagewise exposed resist layer was subjected to developing process using an alkaline developer to dissolved out either the unexposed (negative-working resist) or exposed (positive-working resist) areas. The opened areas on the substrate formed by dissolving out the resist are subjected to additional unselective processing steps to manufacture final integrated circuits or electronic devices.

In manufacturing integrated circuits and the like, the high degree of integration has been intended and, in recent years, in order to attain a higher degree of integration techniques for still more decreasing feature sizes are required. Therefore lithographic techniques using conventional near UV, such as g-line (436 nm) and i-line (365 nm) shift to imaging processes using radiation of shorter wavelength, such as middle UV (350–280 nm), or deep UV (280–150 nm). The latter especially employs KrF (248 nm) or ArF (193 nm) excimer laser radiation. Excimer laser radiation sources emit monochromatic radiation. Highly sensitive, excimer laser compatible chemically amplified, positive- or negative-working deep UV photoresist compositions offering excellent lithographic performance and high resolution capability have become available recently. Due to their chemical compositions and their image formation mechanisms, state-of-the-art chemically amplified photoresist compositions are usually transparent at the exposure wavelength, and do not exhibit a pronounced sensitivity owing to poisoning effects induced by base contaminants present at the photoresist-

substrate or photoresist-air interfaces, respectively. While appropriate deep-UV exposure tools in combination with the high performing photoresists are capable of patterning structural elements with dimensions below quarter micron design rules, tendency of arising image distortions and displacements due to some optical effects become conspicuous in such high resolution image. Therefor the method of forming resist images not affected by such optical effects and having good reproducibility are strongly required.

One of the problems caused by such optical effects is "standing wave" formation which is well known in the art and arise from substrate reflectivity and thin film interference effects of the monochromatic radiation. Another problem is "reflective notching" known in the art due to light reflection effects resulting from highly reflective topographic substrates. In single layer resist processes it is difficult to conduct the linewidth uniformity control due to the reflective notching. Certain reflective topographical features may scatter light through the photoresist film, leading to linewidth variations, or in other case, resist loss. Such problems are extensively documented in the literature, e.g. (i) M. Horn, Solid State Technol., 1991(11), p. 57 (1991), (ii) T. Brunner, Proc. SPIE 1466, p. 297 (1991), or (iii) M. Bolsen et al., Solid State Technol., 1986(2), p. 83, (1986).

Thin film interference generally results in changes of linewidth by variations of the substantial light intensity in the resist film as the thickness of the resist changes. These linewidth variations are proportional to the swing ratio (S) defined by following equation (1) and must be minimized for better linewidth control.

$$S = 4(R_1R_2)^{1/2}e^{-\alpha D} \tag{1}$$

Wherein R_1 is the reflectivity at the resist-air interface, R_2 is the reflectivity of the resist-substrate interface, α is the resist optical absorption coefficient, and D represents the resist film thickness.

One of lithographic techniques to overcome the above-mentioned problems during pattern formation on reflective topography is addition of radiation absorbing dyes to the photoresists as described in U.S. Pat. Nos. 4,575,480 or 4,882,260. This corresponds to an increase of the optical absorption coefficient a in equation (1) above. When a dye is added to the photoresist to form a radiation sensitive film having high optical density at the exposure wavelength, drawbacks such as loss of resist sensitivity, resolution and depth-of-focus capability, contrast deterioration, and profile degradation are encountered. In addition, difficulties during subsequent hardening processes, thinning of the resists in alkaline developers and sublimation of the dye during baking of the films may be observed.

Top surface imaging (TSI) processes, or multi layer resist arrangements (MLR) as described in U.S. Pat. No. 4,370, 405 may help prevent the problems associated with reflectivity. However, such methods require complex processes and are not only difficult to control the processes but also expensive and therefore not preferred. Single layer resist (SLR) processes dominate semiconductor manufacturing because of their simplicity and cost-effectiveness.

The use of either top or bottom anti-reflective coatings in photolithography is a much simpler and effective approach to diminish the problems that arise from thin film interference, corresponding to either a decrease of R_1 or R_2 and thereby reducing the swing ratio S.

The most effective means to eliminate the thin film interference is to reduce the through the use of so-called bottom anti-reflective coatings (BARC). These coatings

have the property of absorbing the light which passes through the photoresist and not reflecting it back. The bottom anti-reflective coating composition is applied as a thin film on the substrate prior to coating with the photoresist composition. The resist is then applied on the bottom anti-reflective coating, exposed and developed. The anti-reflective coating in the resist removed areas is then etched, for example in an oxygen plasma, and the resist pattern is thus transferred to the substrate allowing for further processing steps for forming active elements, interconnecting structures etc. The etch rate of the anti-reflective coating composition is of major importance and should be relatively higher than that of the photoresist, so that it is etched without significant loss of the photoresist film during the etch process.

Bottom anti-reflective coatings are typically divided into two types, namely inorganic and organic bottom anti-reflective coating types.

Inorganic types include stacks of dielectric anti-reflective coatings such as TiN, TiON, TiW and spin-on glasses useful in a thickness range of below 300 Å. Examples are described by (i) C. Noelscher et al., Proc. SPIE 1086, p. 242 (1989), (ii) K. Bather et al., Thin Solid Films, 200, p. 93 (1991), or (iii) G. Czech et al., Microelectr. Engin., 21, p. 51 (1993). Although inorganic dielectric anti-reflective coatings effectively reduce thin film interference effects, they require complicated and precise control of the film thickness, film uniformity, special deposition equipment, complex adhesion promotion techniques prior to resist coating, separate dry etching pattern transfer step, and are usually difficult to remove.

Improved linewidth and standing wave control can also be attained by use of organic bottom anti-reflective coating as same as inorganic type. As organic bottom anti-reflective coatings it is known ones formulated by adding dyes which absorb at the exposure wavelength to a polymer film, as described by C. H. Ting et al., Proc. SPIE 469, p. 24 (1984), or W. Ishii et al., Proc. SPIE 631, p. 295 (1985). Problems of the anti-reflective coatings produced as described above include (1) separation of dye and polymer during spin coating, drying, or baking, (2) sublimation of the dye during the subsequent hard-bake step, (3) dye stripping into resist solvents, (4) thermal diffusion into the resist upon the baking process and (5) interfacial layer formation. These phenomena may cause severe degradation of lithographic properties especially when combined with chemically amplified photoresists and therefore the method of using dye blended bottom anti-reflective coatings are not preferred. Especially problematic is the sublimation issue, as not only the absorption properties of the bottom anti-reflective coating are deteriorated, but also contamination of the expensive equipment must be anticipated, causing process problems due to increased particle concentrations at a later stage.

As an alternative, organic bottom anti-reflective coatings containing radiation absorbing pigments have been suggested (EP-A1 744662). Such bottom anti-reflective coatings may produce a large number of insoluble particles during device processing and thereby reduce yield considerably.

Direct chemical attachment of dyes to a film forming polymer is another option (US patent 5,525247). The materials disclosed therein are usually casted from hazardous organic solvents, such as cyclohexanone or cyclopentanone. M. Fahey et al., Proc. SPIE 2195, p. 422 (1994) describe amino group-containing dyes reacted with the anhydride groups of poly(vinylmethylether-co-maleic anhydride). One problem connected with these types of bottom anti-reflective

coating compositions is that the reaction between the amine and the polymeric anhydride groups does not proceed quantitatively thus resulting in the presence of free amines (EP-A1 583,205, p. 5, lines 17–20). The unreacted amine causes poisoning of the resist at the bottom anti-reflective coating-resist interface especially when base sensitive chemically amplified resist compositions are employed resulting in resist foot formation due to incomplete dissolution of the exposed resist bottom layer upon development. The free dye molecules may also sublime during the baking process, deposit on the fabrication instruments and cause contamination problems as well as health hazard to the workers. One more disadvantage of these specific composition is that imide compounds formed upon the reaction between the amine and the anhydride groups are poor in their solubility and require polar solvents for their processing not used normally in photoresist formulations. From the processing standpoint, it would be ideal to use the same solvent for photoresist and for bottom anti-reflective coating. Furthermore, water which is formed as the by-product of the imidization reaction may cause coating defects (pinholes) during film formation.

Another system which Fahey et al. propose in the above mentioned publication is based on materials composed from copolymers of methyl methacrylate and 9-methylanthracene methacrylate. However, formulations based on these copolymers usually show footing due to the diffusion of photo generated acid into the bottom anti-reflective coating film as well as intermixing of the resist and the bottom anti-reflective coating film thus limiting their practical use. The copolymers are also insoluble in preferred photoresist solvents such as propylene glycol monomethyl ether acetate (PGMEA) or ethyl lactate (EL).

U.S. Pat. Nos. 5,234,990 and 5,578,676 describe polysulfone and polyurea resins which possess inherent light absorbing properties at deep ultraviolet wavelengths. However, these condensation products have comparatively poor film forming properties and therefore exhibit poor step-coverage on topographic substrates, resulting in a problem of image transfer to the substrate. In addition, it has been found that these materials exhibit a high degree of crystallinity and tend to form cracks probably due to their high Tg and rigid structures. Initially, a bottom anti-reflective coating should be soft to achieve good step coverage properties upon coating and in addition should have the ability to crosslink and harden after baking to prevent intermixing of the photoresist with the bottom anti-reflective coating layer as well as diffusion of the photo generated acid.

U.S. Pat. No. 5,554,485 and EP-A1 698823 describe poly(arylether) or poly(arylketone) polymers respectively. These polymers have a rather high concentration of aromatic units and therefore their etch rates are rather low. That is same for the polyvinylnaphthalene derivatives disclosed in U.S. Pat. No. 5,482,817.

EP-A1 542008 describes the use of phenolic type resin binders and melamine type crosslinking agents in combination with either thermal, or photo acid generators to harden the bottom anti-reflective coating film after coating. Such compositions are poor in their storage stability due to the presence of the crosslinking agents and photo acid generators resulting in high film defect yields. In addition, their etch rate is very low due to the presence of rather large amounts of aromatic functional groups.

Japanese Laid-opened Patent Publication No. H10-221855 discloses an anti-reflective coating material composition containing a high molecular compound in which choromophores having 10,000 or more of molar extinction

coefficient for either 365 nm, 248 nm or 193 nm wavelength radiation are linked to at least a part of alcohol moieties of recurrent vinyl alcohol units in main chain and a method of producing resist patterns. However introduction of such bulky polycyclic aromatic group alone into a high molecular compound containing recurrent vinyl alcohol such as polyvinyl alcohol by acetalization reaction requires elevated temperature and long time reaction. In addition it is difficult to attain high reaction percentage. The publication disclose that expected yield is attained when the reaction was conducted in dioxane at 100° C. for 40 hours. However the organic chromophore groups are easy to decompose under such reaction conditions and it is necessary to moderate the reaction conditions.

In summary, a superior bottom anti-reflective coating material should satisfy the following requirements:

a) good film forming property

b) high absorption at the applied exposure wavelength

c) no intermixing with the photoresist

d) high etch rate compared with the photoresist

e) good step coverage on topography

f) practical storage stability

g) compatibility with and solubility in photoresist and edge-bead rinse (EBR) solvents

h) adaptability to several commercial resists

i) ease of production and high yield.

The object of the present invention is to provide an anti-reflective coating composition satisfying above preferable properties, a method of manufacturing integrated circuits using the composition, novel polymer dyes and a method of preparing thereof.

Definitely, the first objective of the present invention is to provide a bottom anti-reflective coating composition which absorbs radiation in the wavelength range of 150–450 nm thus eliminating problems associated with light reflected from the substrate and topography during pattern formation.

The second objective of the present invention is to provide a bottom anti-reflective coating composition having improved adhesion to integrated circuit or micro-electronic substrates, very good coating uniformity and showing no particle formation.

The third objective of the present invention is to provide a bottom anti-reflective coating composition with a superior etch rate than current available bottom anti-reflective coatings, having improved compatibility with the existing chemically amplified photoresists, and generating neither undercut nor footing.

The fourth objective of the present invention is to provide novel polymeric dyes having cyclic acetal moieties and applicable for a bottom anti-reflective coating composition as well as producible easily and in high yield and a method of preparing thereof.

The fifth objective of the present invention is to provide bottom anti-reflective coating compositions comprising of polymeric dyes having cyclic acetal moieties, together with, if necessary, crosslinking agents and other additives such as photo acid generators, plasticizers or surfactants.

The sixth objective of the present invention is to provide novel polymer and copolymer materials producible easily and in high yield, and capable of curing (crosslinking) at the baking temperatures of the resulting bottom anti-reflective coating to harden the bottom anti-reflective coating thus providing a barrier for photoresist solvent or component penetration and thereby preventing foot formation caused by either intermixing or acid diffusion.

The invention further provides a method for application and use of the anti-reflective coating composition in com-

bination with a photoresist on a substrate useful in manufacturing integrated circuits and micro-electronic devices. Thus in a preferred aspect, a method is provided, comprising the steps of; 1) treating a substrate with a primer, 2) applying the bottom anti-reflective composition of the present invention, 3) baking the coated bottom anti-reflective coating film to evaporate the solvent and to harden the film, 4) applying a photoresist on top of the bottom anti-reflective coating, 5) drying the photoresist, 6) exposing the photoresist using a mask, 7) developing the resist and 8) removing the bottom anti-reflective coating in the opened areas.

Other objects will become apparent from the following detailed description, preferred embodiments and illustrative examples mentioned below.

DISCLOSURE OF THE INVENTION

It was found that the objects of the invention described above were able to be attained by using an anti-reflective coating composition comprising at least a solvent and a novel polymer dye with cyclic acetal units.

That is, the present invention provides a bottom anti-reflective coating composition comprising at least a solvent and a polymer dyes as represented by general formula 1:
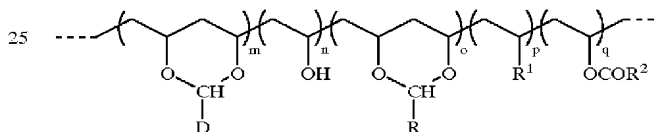
wherein

R represents a hydrogen atom, a substituted or non-substituted C_1–C_{20} alkyl group, a substituted or non-substituted C_6–C_{20} cycloalkyl group, or a substituted or non-substituted C_6–C_{20} aryl group,

R^1 represents a hydrogen atom, a substituted or non-substituted C_1–C_5 alkyl group, a substituted or non-substituted C_1–C_{10} aryl group, or a —$COOR^3$ group in which R^3 represents a C_1–C_{10} alkyl group,

R_2 represents a substituted or non-substituted C_1–C_5 alkyl group, a substituted or non-substituted C_6–C_{20} cycloalkyl group, or a substituted or non-substituted C_6–C_{20} aryl group,

D is an organic chromophore which absorbs at the exposure wavelength (150–450 nm) and represents a substituted or non-substituted C_6–C_{30} aryl group, a substituted or non-substituted C_6–C_{30} condensed aryl group, or a substituted or non-substituted C_4–C_{30} heteroaryl group,

m and o are any integer above zero, and

n, p and q are any integer including zero.

Further the present invention provides a method of forming a bottom anti-reflective coating on a semiconductor substrate such as silicon wafer in which the above mentioned bottom anti-reflective coating composition is spin-coated on the substrate and baked to evaporate the solvent; and a bottom anti-reflective coating formed by the method.

Further the present invention provides a method of manufacturing an integrated circuit in which a positive-working or negative-working photoresist sensitive to radiation in the range of 150 nm-450 nm wavelength is applied onto the above mentioned bottom anti-reflective coating on the substrate, exposed to radiation, developed, and then wet or dry etched to transfer the image.

Further more the present invention provides novel polymer dyes represented by the general formula 1.
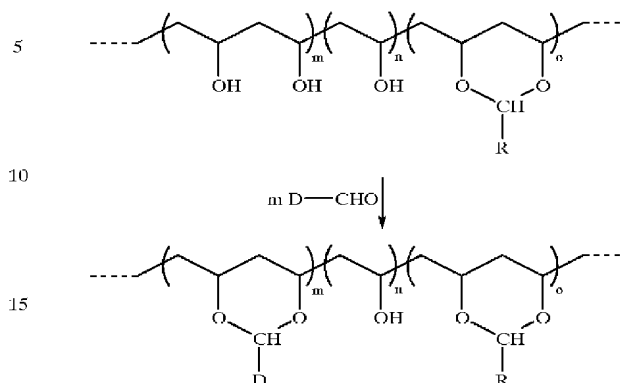
The novel polymer dyes represented by the general formula 1 are prepared by the reaction of polyvinyl alcohol or

derivatives thereof and an aromatic chromophore having an aldehyde group which absorbs the radiation in the range of 150–450 nm wavelength. The film forming composition containing the polymer dye of the invention can absorb radiation in the range of 150–450 nm wavelength. It contains optionally additives such as a crosslinking agent, a thermal or photo acid generator, a plasticizer, and a surfactant. The bottom anti-reflective coating composition of the present invention is utilized for manufacturing integrated circuits due to preventing the problems caused by reflection or scattering of the radiation in lithography process.

The bottom anti-reflective coatings of the present invention are based on radiation absorbing dyes directly attached via cyclic acetal linkages to a vinyl alcohol type polymer backbone. In accordance with the present invention, the polymer dyes represented by the general formula 1 can be synthesized starting from, for example, a partially or fully hydrolyzed polyvinyl alcohol, poly(vinyl alcohol-co-ethylene), poly(vinyl acetal-co-vinyl alcohol), poly(vinyl acetal-co-vinyl alcohol-co-vinyl acetate), or partially hydrolyzed vinyl acetate-co-acrylate block copolymers and the respective chromophore-containing aldehyde compound. Reactions in synthesis examples described below proceed typically in accordance with following reaction schemes. As outlined in reaction scheme 1, polyvinyl alcohol is subjected to the parallel reaction with an aldehyde derivative R—CHO and a radiation absorbing carbonyl chromophore D—CHO. In reaction scheme 2, polyvinyl alcohol partially reacted with an aldehyde is used as the starting material and subsequently reacted with a radiation absorbing chromophore D—CHO:

Reaction scheme 1
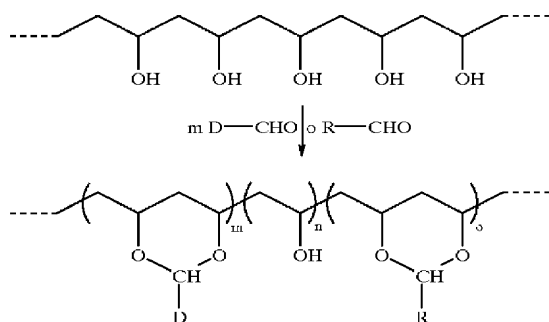
wherein

R represents a hydrogen atom, a substituted or non-substituted C_1–C_{20} alkyl group, a substituted or non-substituted C_6–C_{20} cycloalkyl group, or a substituted or non-substituted C_6–C_{20} aryl group,

D is an organic chromophore which absorbs at the exposure wavelength (150–450 nm) and represents a substituted or non-substituted C_6–C_{30} aryl group, a substituted or non-substituted C_6–C_{30} condensed aryl group, or a substituted or non-substituted C_4–C_{30} heteroaryl group, and m, n and o are integers between 5 and 50,000.

Reaction scheme 2

wherein

R represents a hydrogen atom, a substituted or non-substituted C_1–C_{20} alkyl group, a substituted or non-substituted C_6–C_{20} cycloalkyl group, or a substituted or non-substituted C_6–C_{20} aryl group,

D is an organic chromophore which absorbs at the exposure wavelength (150–450 nm) and represents a substituted or non-substituted C_6–C_{30} aryl group, a substituted or non-substituted C_6–C_{30} condensed aryl group, or a substituted or non-substituted C_4–C_{30} heteroaryl group, and m, n and o are integers between 5 and 50,000.

Both reactions shown in schemes 1 and 2 are classified as acetalization reactions showing the use of aldehydes R—CHO and D—CHO, respectively, as reactants. It is well known to those skilled in the art, that either ketones (ketalization reaction) such as R—CR^4O and D—CR^4O, alkyl acetals (transacetalization reaction) such as R—$CH(OR^5)_2$ and D—$CH(OR^5)_2$, alkyl ketals (transketalization reaction) such as R—$CR^4(OR^5)_2$ and D—$CR^4(OR^5)_2$ or enolethers (wherein R and D have the same meaning as described above, R^4 has the same meaning as R, and R^5 represents a C_1–C_4 alkyl group.) may serve for the same purpose. It should be noted however, that the use of aldehydes is preferred over that of the other compounds mentioned above due to their availability and ease of reaction.

The reactions as shown in schemes 1 and 2 require acid catalysts. Any strong acid such as sulfuric acid, nitric acid or hydrochloric acid can be used. Acidic ion-exchange resins such as Amberlyst (trade name, supplied by Fluka A,G.) may also be applied as catalysts. The use of acidic ion-exchange resins has the advantage of obtaining a final product free from acidic impurities since the catalyst can be removed from the reaction mixture by filtration techniques.

The weight average molecular weight (Mw) of the polyvinyl alcohol used in reaction schemes 1 and 2 may range generally between 500 and 5,000,000. Considering the film forming properties and the solubility characteristics, preferred weight average molecular weights are between 2,000 and 100,000.

Useful radiation absorbing chromophores D include the following groups but are by no means limited to these examples: phenyl, substituted phenyl, benzyl, substituted benzyl, naphthyl, substituted naphthyl, anthracenyl, substituted anthracenyl, anthraquinonyl, substituted anthraquinonyl, acridinyl, substituted acridinyl, azophenyl, substituted azophenyl, fluorenyl, substituted fluorenyl, fluorenonyl, substituted fluorenonyl, carbazolyl, substituted carbazolyl, N-alkylcarbazolyl, dibenzofuranyl, substituted

dibenzofuranyl, phenanthrenyl, substituted phenanthrenyl, pyrenyl, and substituted pyrenyl. The substitutions in the above mentioned dye molecules can include one or more of the following groups: linear, branched or cyclic C_1–C_{20} alkyl, C_6–C_{20} aryl, halogen, C_1–C_{20} alkyloxy, nitro, carbonyl, cyano, amide, sulfonamide, imide, carboxylic acid, carboxylic acid ester, sulfonic acid, sulfonic acid ester, C_1–C_{10} alkylamine, or C_6–C_{20} arylamine.

Suitable examples of R—CHO in reaction scheme 1 include, but are not limited to formaldehyde, acetaldehyde, propionaldehyde, butylaldehyde, benzaldehyde, substituted benzaldehyde, p-hydroxybenzaldehyde, p-methoxybenzaldehyde, and the like.

The selection of the organic solvent in which the reaction between polyvinyl alcohol and the carbonyl compound is performed is not critical provided it is not basic in nature. Preferred solvents include methanol, ethanol, isopropanol, propylene glycol monomethyl ether, ethyl lactate, or glycol. Most preferred is the use of ethanol as the solvent and sulfuric acid as the acid catalyst.

The matters described hereinbefore can be applicable for partially hydrolyzed polyvinyl alcohols containing other recurrent unit except for vinyl alcohol or copolymers containing other recurrent units except for vinyl alcohol and vinyl acetate. By selection of recurrent unit except for vinyl alcohol, regulation control of solubility of polymer dye in solvent, glass transition temperature of polymer dye, melt viscosity of polymer dye, affinity of polymer dye for resist, surface unity in application, or flattening can be conducted.

Some specific examples of monomer forming other recurrent unit containing R^1 group include ethylene, propylene, acrylates such as methylacrylate, styrene, styrene derivatives, and the like. Examples of group R^2 include typically methyl, ethyl, propyl or butyl group and methyl group is preferred.

The molar ratios of the components m and o in the general formula 1 depend on the amount of D—CHO and R—CHO reacted with polyvinyl alcohol. This ratio also determines the absorption coefficient 'k' of the polymer dye as well as its solubility. It is necessary to have a sufficient amount of m in order to obtain bottom anti-reflective coating compositions capable of suppressing the standing waves. The absorption at the targeted wavelength and the refractive index of the final polymer play an important role in the applicability of the material for bottom anti-reflective coatings. Absorption values of the bottom anti-reflective coating in the range of 2 to 40 per micron film thickness is desired and values between 5 and 15 per micron are especially preferred and should be maintained in the copolymers as well. Both, too high absorption and too low absorption may lead to inferior performance of the bottom anti-reflective coating. However, there are no optimum absorption and refractive index values for a bottom anti-reflective coating material as these values also depend on the absorption and refractive index of the photoresist material applied on it. The refractive index of the bottom anti-reflective coating would be optimum if it exactly matches that of the resist layer applied on top. Although the absorption properties of the bottom anti-reflective coating are settled in substance by the molar ratio, the range of the molar ratio may be changed by the molar extinction coefficient of D. The absorption of the anti-reflective coating can be further optimized for a certain wavelength by the selection of suitable substituents on the dye functionality D. Electron withdrawing or electron donating substituents usually shift the absorption wavelength to shorter or longer wavelength, respectively. Similarly, an appropriate choice of substituents on any of the monomer units can enhance the solubility or crosslinking property of the polymer.

When the acetalization reaction is conducted by using aldehyde derivatives, R—CHO and D—CHO described hereinbefore, the uniformity of the reaction mixture is better than that of reaction system not using R—CHO. In addition, the reaction in the mixture solution proceeds at rather low temperature such as about 70° C. and fully for shorter time such as 8–10 hours and the reaction products are obtained in high yield intended. These are preferable from the standpoint of reaction mechanism and protection of chromophores. In the method of producing polymer dyes using two aldehyde derivatives of the present invention, plural chromophores can be bonded to polymer chain. One polymer bonded by plural choromophores can be applicable for two different exposure wavelength radiations. The example thereof is described in Example 7 mentioned below, wherein a polymer dye absorbing at wavelength radiations of both 248 nm KrF laser and 193 nm ArF laser is used. This is clearly different from the technique described in JP-A H10-221855 which does not use aldehyde derivative, R—CHO in production of polymer dyes and is one of main distinctive points of the present invention.

Molar ratios of the components n, p and q in the general formula 1 are any integer containing zero and these values are selected suitably accordance with the properties required to the polymer dye. For example either p or q may be zero or both p and q may be zero.

The preferred examples of the range of these m, n, o, p and q are, m=0.20–0.90, n=0.05–0.30, o=0.01–0.40, p=0–0.40, and q =0.01–0.20.

The solubility of the bottom anti-reflective coating materials in safe solvents is an important criterion. The solvent should be capable to dissolve the polymer dye material and other additives (surfactants, plasticizers, crosslinking agents) to improve the bottom anti-reflective coating film formation properties. From the standpoint of safety, solubility, evaporation ability and film formation, examples of preferred solvents include, but are not limited to propylene glycol monomethyl ether acetate (PGMEA), ethyl lactate (EL), propylene glycol monomethyl ether, cyclohexanone, cyclopentanone, 2-heptanone and combinations thereof. The solubility of the polymer dye represented by general formula 1 of the present invention itself can be controlled by proper selection of suitable coreactants R—CHO as depicted in reaction schemes 1 and 2.

Apart from the polymer dye and the solvent the bottom anti-reflective coating composition of the present invention may also contain surfactants, crosslinking agents, acid generators, and other additives to enhance the performance of the coating, and to form a uniform, defect free film on the semiconductor substrate. As examples of surfactants, fluorinated or siloxane-based compounds can be used but are not limited to these groups of compounds. The crosslinking agents can be either thermal crosslinking agents such as blocked isocyanates, acid catalyzed crosslinking agents such as the melamine or uracil resins, or epoxy-based crosslinking agents. The acid generators can also be either thermal acid generators or photo acid generators.

Another important and desired property of bottom anti-reflective coatings is their high etch rates in plasmas and this property is mainly controlled by the selection of the polymer dye used in the bottom anti-reflective coating material. It is well known in skilled artists in the semiconductor industry that a bottom anti-reflective coating material having significantly higher etch rate than the resist itself in order to successfully transfer the pattern after exposure and further processing steps.

The etch rate of an organic material can be calculated by using the Ohnishi number or the carbon/hydrogen ratio of

the polymer. Since the polymer materials represented by the general formula 1 contain a high oxygen content and aliphatic carbon moieties, these compounds exhibit high Ohnishi numbers and are anticipated to have high etch rates. This is another merit of this kind of polymer dyes when used as a bottom anti-reflective coating material.

The glass transition temperature of the bottom anti-reflective coating material plays an important role with respect to substrate coverage and intermixing properties between the bottom anti-reflective coating layer and the applied photoresist. While a relative low glass transition temperature is preferred to achieve good step coverage, a higher glass transition point is preferred with regard to non-intermixing properties between the bottom anti-reflective coating and photoresist layer. Since the photoresist is applied onto the bottom anti-reflective coating layer, exposed and developed, any mixing between the alkali-insoluble bottom anti-reflective coating layer and the alkali-soluble photoresist would lead to incomplete removal of the photoresist material upon development usually performed with alkaline developers. Another problem to encounter is that when a chemically amplified photoresist material is applied on a bottom anti-reflective coating with low glass transition temperature the acid formed upon exposure might diffuse into the bottom anti-reflective coating layer leading to a distortion of the latent acid image and causing incomplete removal of the photoresist material upon development. Therefore, it is desirable that the bottom anti-reflective coating material has a glass transition temperature at least above the maximum processing temperatures used while applying the photoresist. This can be controlled in the present invention by manipulating the molar ratio of m, n and o.

The polymer dye content in the anti-reflective coating composition is preferably in the range of about 1 wt % to about 30 wt %. Preferred concentration is definitely dependent on the molecular weight of the dye polymer and the film thickness required to the bottom anti-reflective coating. The anti-reflective coating is applied on the substrate using techniques well known to those skilled in the art, such as dipping, spin coating, roller coating or spraying. The preferred film thickness of the anti-reflective coating ranges from 30 nm to 1000 nm.

The process of the present invention further comprises coating a substrate with the bottom anti-reflective coating of the present invention and heating on a hotplate or convection oven at a sufficiently high temperature for a sufficient length of time to remove the solvent in the coating and to crosslink the polymer to a sufficient extent so as not to be soluble in the coating solvent of the photoresist or in the alkaline developer. The preferred ranges of temperature and time upon baking are from about 70° C. to about 280° C. and for 30 seconds to 30 minutes. If the temperature is below 70° C. the residual amount of solvent is too high or the degree of crosslinking is insufficient. At temperatures above 280° C. the polymer may become chemically unstable.

The bottom anti-reflective coating is coated on top of the substrate and is further subject to heating and dry etching. It is envisioned that the bottom anti-reflective coating is of sufficiently low metal ion content so that the electrical properties of the semiconductor device are not adversely affected. Treatments such as passing a solution of the polymer through an ion exchange column, filtration and extraction can be used to reduce the concentrations of metal ions or particles.

In the present invention integrated circuits are produced by the way that positive- or negative-working photoresist

sensitive to radiation in the range of 150 nm–450 nm wavelength is applied onto the bottom anti-reflective coating layer formed by applying the bottom anti-reflective coating composition of the present invention on the substrate. After this, the resist layer on the substrate is subjected to exposure and development, and then the image is transferred by wet or dry etching followed by processing necessary for forming the integrated circuit.

The bottom anti-reflective coating materials of the present invention can be preferably applied for both positive- and negative-working resist materials. The preferred photoresists include but are by no means limited to these examples, one comprising a novolak resin and a photosensitizer such as quinondiazide and one comprising a substituted polyhydroxystyrene and a photo active agent.

BEST MODE FOR CARRYING OUT THE INVENTION

The bottom anti-reflective coating composition of the present invention, the method of manufacturing the composition and the manner of using the composition are described in more detail by way of following Application Example and Examples but these examples are only illustrative and not intended to limit or restrict the scope of the invention in any way and should not be construed as providing conditions, parameters or values which must be utilized exclusively in order to practice the present invention.

APPLICATION EXAMPLE

The following general method was used to evaluate the bottom anti-reflective coating compositions of the present invention unless specified otherwise:

A 2 wt % solution of the bottom anti-reflective coating material in an appropriate solvent was filtered using 0.5 and 0.2 micron filters, and spin-coated on a 4-inch silicon wafer at a suitable spin speed for 40 seconds in such a way that the bottom anti-reflective coating composition has a film thickness of 60 nm after baking at 200° C. for 60 seconds. The film was checked with a high resolution microscope to identify surface defects. The values of the optical constants n (refractive index) and k (absorption parameter) of the film were measured on a ellipsometer at the respective wavelengths (248 nm or 356 nm).

Then a positive- or negative-working, acid-catalyzed deep UV photoresist (film thickness approximately 700 nm) or a positive- or negative-working i-line novolak resist (film thickness approximately 1000 nm) was applied on the bottom anti-reflective coating by spin-coating at a suitable spin speed for 40 seconds. Depending on the resist material, the resists were soft baked for 60 seconds at 90–110° C. and exposed on a stepper operating with an excimer laser (248 nm) source in the case of the deep UV resists or an i-line (356 nm) stepper in the case of the i-line resist using a reticle with line and space patterns. Following the exposure, the deep UV resists were subjected to a post-exposure bake at 90–110° C. The photoresists were developed using a 0.26 N tetramethyl ammonium hydroxide developer solution for 60 seconds at 23° C. to form the resist patterns. The resist patterns were examined on a scanning electron microscopy to check the resolution, standing wave formation, reflective notching, and footing. In order to evaluate the step-coverage properties of the bottom anti-reflective coating materials, a silicon substrate was first coated with a conventional i-line photoresist at a film thickness of 1000 nm, imagewise exposed, developed and hard-baked at 200° C. Then the bottom anti-reflective coating material was coated on the

processed wafer having 1000 nm steps provided by the imaged photoresist. The step-coverage of the bottom anti-reflective coating then was analyzed by a scanning electron microscopy. The etch rates of the bottom anti-reflective coating materials were evaluated using oxygen and fluoride gas plasmas.

Example 1

Synthesis of a polymer dye starting from polyvinyl alcohol (PVA), anthracene-9-aldehyde (9-AA) and propionaldehyde (PA) and application thereof as a bottom anti-reflective coating

22.0 g (0.5 mol) of polyvinyl alcohol (supplied from Wako Pure Chemical, degree of polymerization DP=500), 150 g of ethanol, 25.78 g (0.125 mol) of anthracene-9-aldehyde, 7.26 g (0.125 mol) of propionaldehyde, 0.15 g of 2,6-di-t-butyl-4-methylphenol and 0.25 g of concentrated sulfuric acid were charged into a 300 ml flask. With stirring, the mixture was heated at 70° C. for 8 hours under nitrogen atmosphere. The resulting mixture was cooled and the precipitated solid was filtered, dissolved in tetrahydrofuran (THF), and precipitated from THF in water twice. The resulting yellow powder was dried at 40° C. under vacuum (1 torr). The k value of the polymer as measured on an ellipsometer at 248 nm was found to be 0.4. The polymer was dissolved in cyclohexanone (2 wt % solids), filtered and applied as bottom anti-reflective coating as described in Application Example. A positive-working deep UV resist AZ® DX 1100 available from Clariant (Japan) K.K., was spin-coated, and softbaked at 110° C. to yield a film thickness of 755 nm and then exposed using a deep UV stepper (Nikon EX-10B) attached with a 248 nm KrF laser at a dose of 52 mJ/cm². The exposed wafer was baked at 90° C. for 60 seconds, developed using paddle development for 60 seconds at 23° C., rinsed and dried.

Scanning electron microscope inspection of the line and space patterns revealed that no standing waves are noticed due to the suppression of reflected light from the substrate by the polymer dye. The resist line pattern profiles were found to be vertical, and the spaces were almost clear showing neither scum nor residues. An etch rate of the bottom anti-reflective coating using an oxygen and trifluoromethane gas plasma at 60 W was found to be 100 nm/minute.

Examples 2

The procedure of Example 1 was repeated except that positive-working deep Uv photoresist AZ® DX 1200P available from Clariant (Japan) K.K. was used as deep UV photoresist and prebake 90° C., film thickness 970 nm, dose 28 mJ/cm², and post exposure bake 105° C. were adapted as process conditions.

The resulting pattern showed neither footing of the lines nor scum in the spaces, and their profiles were smooth due to the absence of standing waves.

Example 3

The procedure of Example 1 was repeated except that positive-working deep UV photoresist AZ® DX 1300P available from Clariant (Japan) K.K. was used as deep UV photoresist and prebake 90° C., film thickness 715 nm, dose 13 mJ/cm², and post exposure bake 110° C. were adapted as process conditions.

The resulting pattern showed neither footing of the lines nor scum in the spaces, and their profiles were smooth due to the absence of standing waves.

Example 4

Synthesis of a polymer dye starting from polyvinyl alcohol, anthracene-9-aldehyde and propionaldehyde and application thereof as a bottom anti-reflective coating

22.0 g (0.5 mol) of polyvinyl alcohol (supplied from Wako Pure Chemical Co., degree of polymerization 500), 150 g of ethanol, 25.78 g (0.125 mol) of anthracene-9-aldehyde, 7.26 g (0.125 mol) of propionaldehyde, 0.15 g of 2,6-di-t-butyl-4-methylphenol and 1.20 g of Amberlyst 15 (acidic type ion-exchange resin from Fluka A.G., catalyst) were charged into a 300 ml flask. The mixture was stirred and heated at 70° C. for 8 hours under nitrogen atmosphere. After the solution was cooled to room temperature, the solid phase was filtered off and dissolved in tetrahydrofuran (THF). The insoluble portion consisting mainly of Amberlyst 15 was removed and the THF solution was twice precipitated from THF in water. The polymer dye was dried at 40° C. under vacuum (1 torr). The k value of the polymer as measured on an ellipsometer at 248 nm was found to be 0.39. The polymer was dissolved in cyclohexanone (2 wt % solids), filtered and coated as a bottom-anti-reflective coating as described in Application Example. A positive-working deep UV resist AZ® DX 1100 available from Clariant (Japan) K.K. was spin-coated and processed as described in Example 1.

The obtained line and space patterns were found to be free from standing wave. The pattern profiles were found to be straight, and the space were found to be clear with no scum or residues. An etch rate of the bottom anti-reflective coating using oxygen and trifluoromethane gas plasma at 60 W was found to be 100 nm/minute.

Examples 5

The procedure of Example 4 was repeated except that positive-working deep UV photoresist AZ® DX 2034P available from Clariant (Japan) K.K. was used as deep UV resist and prebake 90° C., film thickness 570 nm, dose 34 mJ/cm², and post-exposure bake 105° C. were adapted as process conditions.

The resulting pattern showed neither footing of the lines nor scum in the spaces, and their profiles were smooth due to the absence of standing waves. The resolution of the deep UV photoresist AZ® DX 2034P on this bottom anti-reflective coating was better than 0.20 μm.

Example 6

The procedure of Example 4 was repeated except that positive-working deep UV photoresist APEX® E avilable from Shipley Corp. was used as deep UV resist and prebake 90° C., film thickness 725 nm, dose 11 mJ/cm², and post-exposure bake 110° C. were adapted as process conditions.

The resulting pattern showed neither footing of the lines nor scum in the spaces, and their profiles were smooth due to the absence of standing waves.

Example 7

Synthesis of a polymer dye starting from polyvinyl alcohol, anthracene-9-aldehyde and 4-hydroxybenzaldehyde (4-HBA) and application thereof as a bottom anti-reflective coating

22.0 g (0.5 mol) of polyvinyl alcohol (supplied from Wako Pure Chemical Co., degree of polymerization 500), 150 g of ethanol, 25.78 g (0.125 mol) of anthracene-9-aldehyde, 13.43 g (0.125 mol) of 4-hydroxybenzaldhyde, 0.15 g of 2,6-di-t-butyl-4-methylphenol and 0.25 g of concentrated sulfuric acid were charged into a 300 ml flask. The mixture was stirred and heated at 70° C. for 8 hours under nitrogen atmosphere. The solution was cooled to room temperature, the solid phase was filtered off and was dissolved in tetrahydrofuran (THF). Insoluble portions were

removed and the THF solution was precipitated from THF twice in water. The product was dried at 40° C. under vacuum (1 torr). The k value of the polymer as measured on an ellipsometer at 248 nm was found to be 0.32. The polymer was dissolved in cyclohexanone (2 wt % solids), filtered and coated as bottom anti-reflective coating as described in Application Example. A positive-working deep UV resist AZ® DX 1100 available from Clariant (Japan) K.K. was spin-coated on the bottom anti-reflective coating and processed as described in Example 1.

The bottom anti-reflective coating used in this Example is applicable not only for exposure with 248 nm KrF laser but also for that with 193 nm ArF laser. The k value of the polymer as measured on an ellipsometer at 193 nm was found to be 0.32.

The obtained line and space patterns were found to be free from standing waves due to the suppression of reflected light from the substrate. The pattern profiles were found to be straight, and the spaces were found to be clear with neither scum nor residues. An etch rate of the bottom anti-reflective coating using oxygen and trifluoromethane gas plasma at 60 W was found to be 90 nm/minute.

Examples 8

The procedure of Example 7 was repeated except that negative-working deep UV photoresist TDUR® N9 available from Tokyo Ohka K. K. was used in place of deep UV resist AZ® DX1100 and prebake 100° C., film thickness 730 nm, dose 44 mJ/cm², and post-exposure bake 130° C. were adapted as process conditions.

Example 9

The procedure of Example 7 was repeated except that positive-working deep UV photoresist UVIII® available from Shipley Corp. was used in place of deep UV resist AZ® DX1100 and prebake 130° C., film thickness 625 nm, dose 21 mJ/cm², and post-exposure bake 130° C. were adapted as process conditions.

Example 10

The procedure of Example 7 was repeated except that positive-working i-line and deep UV photoresist AZ® PR1024 available from Clariant Corp. was used in place of deep UV resist AZ® DX1100 and prebake 90° C., film thickness 350 nm, dose of deep UV 32 mJ/cm², and no post-exposure bake were adapted as process conditions.

All resulting patterns in Examples 8, 9 and 10 showed neither footing of the lines nor scum in the spaces, and their profiles were smooth due to the absence of standing waves.

Example 11

Synthesis of a polymer dye starting from 80% hydrolyzed polyvinyl alcohol, anthracene-9-aldehyde and propionaldehyde and application thereof as a bottom anti-reflective coating

25 g of polyvinyl alcohol (supplied from Aldrich A.G., weight average molecular weight Mw=9,000–10, 000 and hydrolysis degree 80%), 150 g of ethanol, 25.78 g (0.125 mol) of anthracene-9-aldehyde, 7.26 g (0.125 mol) of propionaldehyde, 0.15 g of 2,6-di-t-butyl-4-methylphenol and 0.25 g of concentrated sulfuric acid were charged into a 300 ml flask. The mixture was stirred and heated at 70° C. for 8 hours under nitrogen atmosphere. After the solution was cooled, it was diluted with ethanol. The solid phase was filtered off and dissolved in THF. The THF solution was twice precipitated in water. The polymer dye obtained was

dried at 40° C. under vacuum (1 torr). The k value of the polymer as measured on an ellipsometer at 248 nm was found to be 0.35. The polymer was dissolved in ethyl lactate (2 wt % solids), filtered and coated as a bottom-anti-reflective coating as described in Application Example. A positive-working deep UV resist AZ® DX 1100 available from Clariant (Japan) K.K. was spin-coated and processed as described in Example 1. The resulting pattern showed neither standing wave in the lines nor scum or residues in the spaces.

Example 12

Negative-working deep UV resist with following constitution was applied on the bottom anti-reflective coating described in Example 11.

(constitution)	(part by weight)
4-hydroxystyrene/styrene (8/2) copolymer (weight average molecular weight 12,000)	80
hexamethoxymethylmeramine (distilled)	20
tribromomethylphenylsulfone	1
tributyl amine	0.1

The resist applied on the substrate was soft-baked for 60 seconds at 110° C., exposed at dose of 24 mJ/cm², post-exposed at 120° C. for 60 seconds and processed as described in Example 1. Under these conditions some scum (footing) in the unexposed areas was observed. Therefore, a 5 wt % Kronate® thermal crosslinking agent (available from Nippon Polyurethane K. K.) was added to the bottom anti-reflective coating solution described in Example 11 and the resultant composition was used in place of the bottom anti-reflective coating composition described in Example 11 and processed as described above. This time, the line and space patterns were found to be free from standing waves. The pattern profiles were found to be straight and the space was found to be clear with no scum.

An etch rate of the bottom anti-reflective coating using oxygen and trifluoromethane gas plasma at 60 W was found to be 105 nm/minute. Example 13: Synthesis of a polymer dye starting from poly(vinyl alcohol-co-ethylene) [PVA-ET], anthracene-9-aldehyde and propionaldehyde and application thereof as a bottom anti-reflective coating

22 g of poly(vinyl alcohol-co-ethylene) (obtained from Aldrich Co., ethylene content 27 mol %), 150 g of o-xylene, 25.78 g (0.125 mol) of anthracene-9-aldehyde, 3.6 g (0.063 mol) of propionaldehyde, 0.15 g of 2,6-di-t-butyl-4-methylphenol and 0.25 g of concentrated sulfuric acid were charged into a 300 ml flask. The mixture was stirred and heated at 120° C. for 8 hours under nitrogen atmosphere. The solution was cooled, diluted, and filtered. The viscous solution obtained was twice precipitated in a 70:30 v/v ethanol:water mixture. The polymer was dried at 40° C. under vacuum (1 torr). The k value of the polymer as measured on an ellipsometer at 248 nm was found to be 0.38. The polymer was dissolved in ethyl lactate (2 wt % solids), filtered and coated as bottom-anti-reflective coating as described in the general application example. A positive-working deep UV resist AZ® DX 1100 available from Clariant (Japan) K.K. was spin-coated on the bottom anti-reflective coating and processed as described in Example 1.

The obtained line and space patterns were found to be free from standing waves due to suppression of reflected light from the substrate. The pattern profiles were found to be straight and the space was found to be clear with no scum or residues.

Similar results were obtained with the positive-working deep UV photoresist AZ® DX 2034 as well as a negative-working resist described in Example 12. An etch rate of the bottom anti-reflective coating material using oxygen and trifluoromethane gas plasma at 60 W was found to be 90 nm/minute.

Comparative Example 1

Synthesis of a polymer dye starting from polyvinyl alcohol and anthracene-9-aldehyde and application thereof as a bottom anti-reflective coating

22.0 g (0.5 mol) of polyvinyl alcohol (supplied from Wako Pure Chemical Co., degree of polymerization 500), 150 g of ethanol, 25.78 g (0.125 mol) of anthracene-9-aldehyde, 0.15 g 2,6-di-t-butyl-4-methylphenol and 0.25 g of concentrated sulfuric acid were charged into a 300 ml flask. The mixture was stirred and heated at 70° C. for 8 hours under nitrogen atmosphere. The resulting mixture was cooled and the precipitated solid was filtered and dissolved in tetrahydrofuran (THF). Small amount of insoluble portion was removed and the THF solution was precipitated from THF in water twice. The resulting yellow powder was dried at 40° C. under vacuum (1 torr). The k value of the polymer as measured on an ellipsometer at 248 nm was found to be 0.42. The polymer was dissolved in cyclohexanone (2 wt % solids), filtered and coated as bottom anti-reflective coating as described in Application Example. A positive-working deep UV resist AZ® DX 1100 available from Clariant (Japan) K. K. was spin-coated on the anti-reflective coating and processed as described in Example 1.

In the line and space patterns no standing waves was observed due to the suppression of reflected light from the substrate. The resist pattern profiles were found to be vertical, and the spaces were clear showing neither scum nor residues. An etch rate of the bottom anti-reflective coating using an oxygen and trifluoromethane gas plasma at 60 W was found to be 105 nm/minute.

Comparative Example 2

The procedure of Comparative Example 1 was repeated except that polyvinyl alcohol (supplied from Wako Pure

Chemical Co., degree of polymerization 1000) was used in the synthesis in place of polyvinyl alcohol (supplied from Wako Pure Chemical Co., degree of polymerization 500).

Comparative Example 3

The procedure of Comparative Example 1 was repeated except that partially hydrolyzed polyvinyl alcohol (supplied from Wako Pure Chemical Co., degree of polymerization 1000) was used in the synthesis in place of polyvinyl alcohol (supplied from Wako Pure Chemical Co., degree of polymerization 500).

Comparative Example 4

The procedure of Comparative Example 1 was repeated except that partially hydrolyzed polyvinyl alcohol (supplied from Wako Pure Chemical Co., degree of polymerization 2800) was used in the synthesis in place of polyvinyl alcohol (supplied from Wako Pure Chemical Co., degree of polymerization 500).

Comparative Example 5

The procedure of Comparative Example 1 was repeated except that partially hydrolyzed polyvinyl alcohol (supplied from Wako Pure Chemical Co., degree of polymerization 3500) was used in the synthesis in place of polyvinyl alcohol (supplied from Wako Pure Chemical Co., degree of polymerization 500).

In all cases of Comparative Examples 2 to 5 neither footing of the lines nor scum in the spaces were observed, and the photoresist profiles were smooth due to the absence of standing waves. However, it was found that the step coverage properties became inferior in proportion to the increase of degree of polymerization. As the result, it was seen that the polymer dye formed using higher degree of polymerization polymer showed a tendency of inferior film formation along the stepped surface.

Yields of acetalization reactions in Examples 1, 4, 7, 11 and 13 and Comparative Examples 1 to 5 are shown in following table 1.

TABLE 1

	Backbone polymer	D-CHO	R-CHO	Reaction temperature (° C.)	Reaction time (hour)	Yield* (%)	Special mention
Example 1	PVA DP = 500	9-AA	PA	70	8	116	
Example 4	PVA DP = 500	9-AA	PA	70	8	132	
Example 7	PVA DP = 500	9-AA	4-HBA	70	8	126	
Example 11	PVA Mw = 9000~10000 80% hydrolyzed	9-AA	PA	70	8	118	
Example 13	PVA-Et (Et = 27 mol %)	9-AA	PA	120	8	128	
Comparative Example 1	PVA DP = 500	9-AA	—	70	8	60	Separation of solid phase and liquid phase was difficult
Comparative Example 2	PVA DP = 1000	9-AA	—	70	8	78	Separation of solid phase and liquid phase was difficult
Comparative Example 3	PVA DP = 1000 Partially saponified	9-AA	—	70	8	100	Separation of solid phase and liquid phase was difficult
Comparative Example 4	PVA DP = 2800 Partially saponified	9-AA	—	70	8	82	Separation of solid phase and liquid phase was difficult

TABLE 1-continued

	Backbone polymer	D-CHO	R-CHO	Reaction temperature (° C.)	Reaction time (hour)	Yield* (%)	Special mention
Comparative Example 5	PVA DP = 3500 Partially saponified	9-AA	—	70	8	80	Separation of solid phase and liquid phase was difficult

*wt % based on weight of charged PVA

It is clearly understood from table 1 that the yield of reaction product using both an alkyl or benzaldehyde derivative and anthracene-9-aldehyde is higher than that using only anthracene-9-aldehyde.

Effect of the Invention

In the present invention solvents used in formation of the photoresist layer can be utilized as a solvent of the bottom anti-reflective coating composition, and the bottom anti-reflective coating composition of the present invention has good storage stability, excellent film formation properties and excellent step coverage properties. In addition, since the bottom anti-reflective coating formed by using the bottom anti-reflective coating composition of the present invention reveals high absorption at exposure wavelength radiation, there is no problem of standing wave formation or reflective notching as well as intermixing between the photoresist layer and the bottom anti-reflective coating. Further the bottom anti-reflective coating of the present invention has high etch rate. Therefore fine resist patterns with high resolution and good pattern shape can be formed by using the bottom anti-reflective coating composition of the present invention and integrated circuits having desirable degree of integration can be manufactured with ease by processing the semiconductor substrate with the fine resist patterns.

Industrial applicability

As has been described hereinbefore, the novel polymer dyes of the present invention can be used as bottom anti-reflective coating materials and by use of the bottom anti-reflective coating composition comprising the novel polymer dye, integrated circuits with high degree of integration can be formed easily and in high yield.

What is claimed is:

1. A bottom anti-reflective coating composition for use in photolithography which comprises at least a solvent and a polymer dye represented by general formula 1:
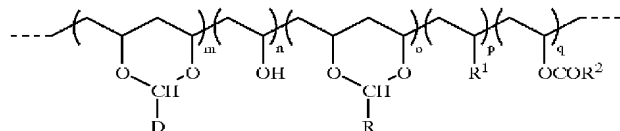
wherein

R represents a hydrogen atom, a substituted or non-substituted C_1–C_{20} alkyl group, a substituted or non-substituted C_6–C_{20} cycloalkyl group, or a substituted or non-substituted C_6–C_{20} aryl group,

R^1 represents a hydrogen atom, a substituted or non-substituted C_1–C_5 alkyl group, a substituted or non-substituted C_6–C_{10} aryl group, or a —COOR^3 group in which R^3 represents a C_1–C_{10} alkyl group,

R^2 represents a substituted or non-substituted C_1–C_5 alkyl group, a substituted or non-substituted C_6–C_{20} cycloalkyl group, or a substituted or non-substituted C_6–C_{20} aryl group,

D is an organic chromophore which absorbs at the exposure wavelength (150–450 nm) and represents a substituted or non-substituted C_6–C_{30} aryl group, a substituted or non-substituted C_6–C_{30} condensed aryl group, or a substituted or non-substituted C_4–C_{30} heteroaryl group,

m and o are any integer above zero, and

n, p and q are any integer including zero.

2. The bottom anti-reflective coating composition according to claim 1 wherein D represents phenyl, substituted phenyl, benzyl, substituted benzyl, naphthyl, substituted naphthyl, anthracenyl, substituted anthracenyl, anthraquinonyl, substituted anthraquinonyl, acridinyl, substituted acridinyl, azophenyl, substituted azophenyl, fluorenyl, substituted fluorenyl, fluorenonyl, substituted fluorenonyl, carbazolyl, substituted carbazolyl, N-alkylcarbazolyl, dibenzofuranyl, substituted dibenzofuranyl, phenanthrenyl, substituted phenanthrenyl, pyrenyl, or substituted pyrenyl, and the substitution is optionally selected from one or more of the following groups; linear, branched or cyclic C_1–C_{20} alkyl, C_6–C_{20} aryl, halogen, C_1–C_{20} alkyloxy, nitro, carbonyl, cyano, amide, sulfonamide, imide, carboxylic acid, carboxylic acid ester, sulfonic acid, sulfonic acid ester, C_1–C_{10} alkylamine, or C_6–C_{20} arylamine.

3. The bottom anti-reflective coating composition according to claim 1 wherein R represents either hydrogen, methyl, ethyl, propyl, butyl, nitrophenyl, hydroxyphenyl, or methoxyphenyl.

4. The bottom anti-reflective coating composition according to claim 1 wherein R^2 represents methyl, ethyl, propyl, phenyl, naphthyl, or anthracenyl.

5. The bottom ant-reflective coating composition according to claim 1 wherein D represents substituted or non-substituted phenyl, naphthyl or anthracenyl.

6. The bottom anti-reflective coating composition according to claim 5 wherein p is zero.

7. The bottom anti-reflective coating composition according to claim 1 wherein the polymer dye represented by the general formula 1 has a weight average molecular weight (Mw) between 2,000 to 200,000.

8. The bottom anti-reflective coating composition according to claim 1 wherein 50 to 95 parts by weight of the solids are the polymer dye represented in the general formula 1 and 50 to 5 parts by weight are a thermal crosslinking agent.

9. The bottom anti-reflective coating composition according to claim 8 wherein the crosslinking agent is either melamine, blocked isocyanate, uracil, or epoxy type crosslinking agent.

10. The bottom anti-reflective coating composition according to claim 1 wherein 50 to 95 parts by weight of the solids are the polymer dye represented by the general formula 1, 50 to 5 parts by weight are a thermal crosslinking agent and 1 to 10 parts by weight of solids are an acid generator.

11. The bottom anti-reflective coating composition according to claim 10 wherein the crosslinking agent is

either melamine, blocked isocyanate, uracil, or epoxy type crosslinking agent and the acid generator is either an onium salt, a diazomethane compound or a nitrobenzyl tosylate.

12. The bottom anti-reflective coating composition according to claim **1** wherein the polymer dye represented by the general formula 1 are dissolved in 1 to 10 wt % concentration in cyclohexanone, propylene glycol monomethyl ether acetate, ethyl lactate, methyl amyl ketone, or a mixture of these solvents.

13. A method of producing an anti-reflective coating on a semiconductor substrate which comprises the following steps:

a) dissolving at least the polymer dye represented by the general formula 1 described in claim **1** in an organic solvent,

b) filtering the solution and then spin-, spray-, dip-, or roller-coating the solution onto a semiconductor substrate, and

c) thermally removing the solvent to form a substrate coated with a bottom anti-reflective coating composition described in claim **1**.

14. A method of manufacturing integrated circuits in which a positive- or negative-working photoresist sensitive to radiation in the range of 150 nm to 450 nm is applied on a semiconductor substrate coated with a thin layer of a bottom anti-reflective coating composition of claim **1**, and the resist coated substrate is exposed with radiation, developed, and etched by dry or wet etching process to transferred the image on to the substrate.

15. The method of manufacturing integrated circuits according to claim **14** wherein the photoresist comprises a novolak resin, a photosensitive compound and a solvent.

16. The method of manufacturing integrated circuits according to claim **14** wherein the photoresist comprises a substituted polyhydroxystyrene, a photo-active compound and a solvent.

17. A polymer dye represented by general formula 1:
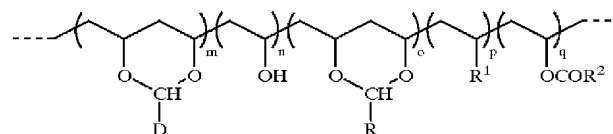
wherein

R represents a hydrogen atom, a substituted or non-substituted C_1–C_{20} alkyl group, a substituted or non-substituted C_6–C_{20} cycloalkyl group, or a substituted or non-substituted C_6–C_{20} aryl group,

R^1 represents a hydrogen atom, a substituted or non-substituted C_1–C_5 alkyl group, a substituted or non-substituted C_6–C_1 aryl group, or a —$COOR^3$ group in which R^3 represents a C_1–C_{10} alkyl group,

R^2 represents a substituted or non-substituted C_1–C_5 alkyl group, a substituted or non-substituted C_6–C_{20} cycloalkyl group, or a substituted or non-substituted C_6–C_{20} aryl group,

D is an organic chromophore which absorbs at the exposure wavelength (150–450 nm) and represents a substituted or non-substituted C_6–C_{30} aryl group, a substituted or non-substituted C_6–C_{30} condensed aryl group, or a substituted or non-substituted C_4–C_{30} heteroaryl group,

m and o are any integer above zero, and

n, p and q are any integer including zero.

18. A method of producing the polymer dye represented by the general formula 1 described in claim **17**.

* * * * *

(12) **United States Patent**　(10) **Patent No.:**　**US 6,399,686 B1**
Puligadda et al.　(45) **Date of Patent:**　**Jun. 4, 2002**

(54) **ANTI-REFLECTIVE COATING COMPOSITIONS COMPRISING POLYMERIZED AMINOPLASTS**

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(73) Assignee: **Brewer Science, Inc.**, Rolla, MO (US)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

(21) Appl. No.: **09/691,774**

(22) Filed: **Oct. 18, 2000**

Related U.S. Application Data

(62) Division of application No. 09/552,236, filed on Apr. 19, 2000, now Pat. No. 6,323,310.

(51) **Int. Cl.^{7}** **B05D 3/02**
(52) **U.S. Cl.** **524/284;** 427/385.5
(58) **Field of Search** 524/284; 427/385.5

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Primary Examiner—Erma Cameron
(74) *Attorney, Agent, or Firm*—Hovey Williams LLP

(57) **ABSTRACT**

Improved anti-reflective coating compositions for use in integrated circuit manufacturing processes and methods of forming these compositions are provided. Broadly, the compositions are formed by heating a solution comprising a compound including specific compounds (e.g., alkoxy alkyl melamines, alkoxy alkyl benzoguanamines) under acidic conditions so as to polymerize the compounds and form polymers having an average molecular weight of at least about 1,000 Daltons. The monomers of the resulting polymers are joined to one another via linkage groups (e.g., —CH$_2$—,—CH$_2$—O—CH$_2$—) which are bonded to nitrogen atoms on the respective monomers. The polymerized compound is mixed with a solvent and applied to a substrate surface after which it is baked to form an anti-reflective layer. The resulting layer has high k values and can be formulated for both conformal and planar applications.

17 Claims, 3 Drawing Sheets

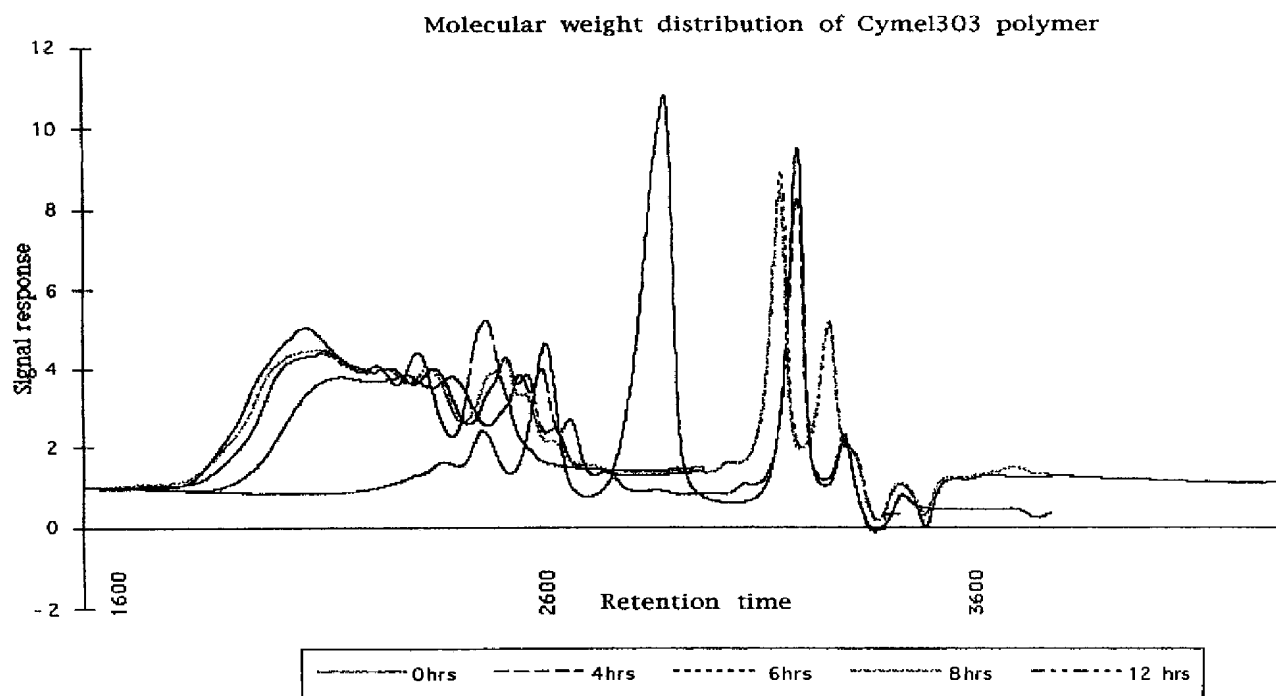Molecular weight distribution of Cymel303 polymer

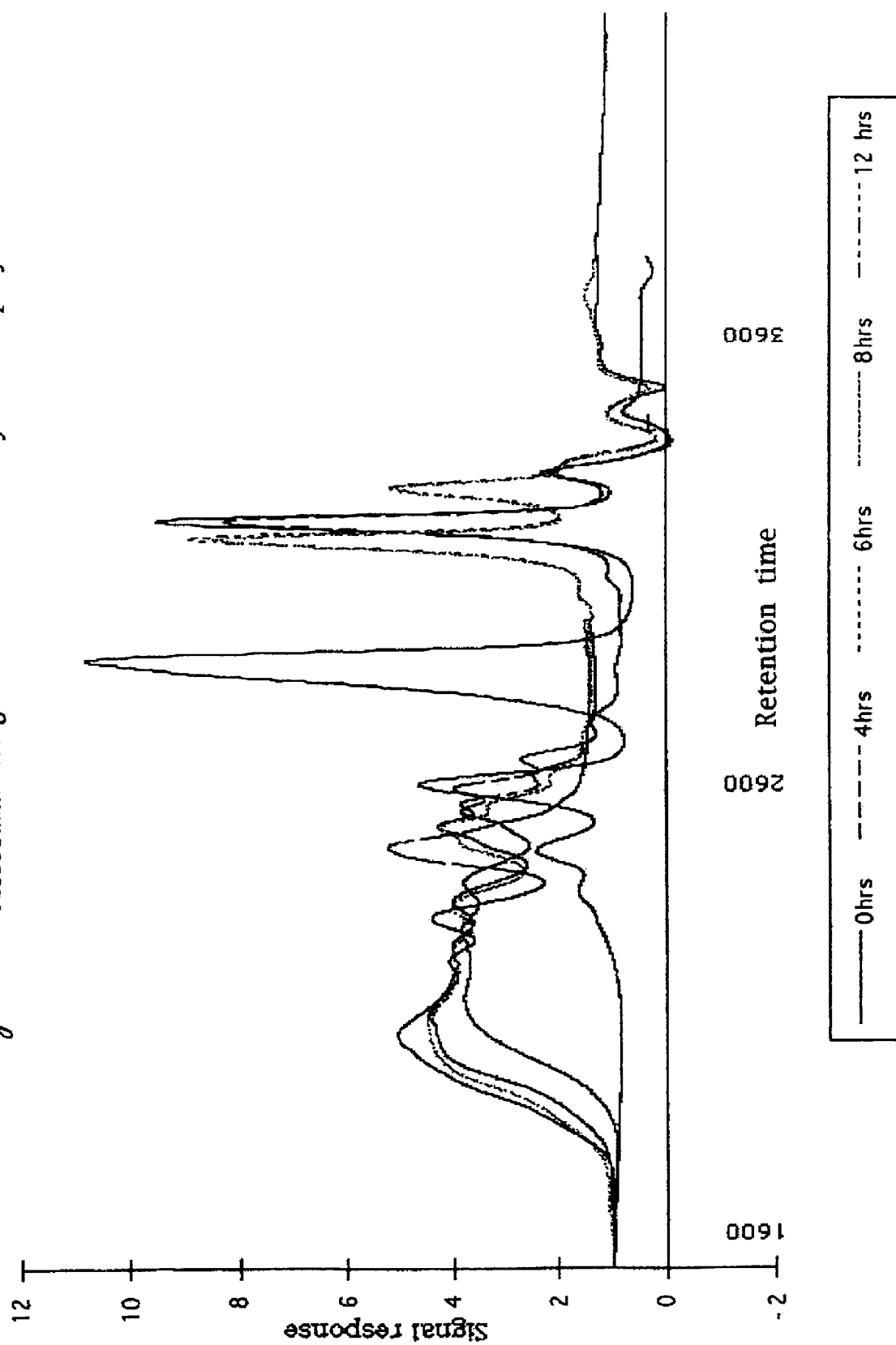Fig. 1   Molecular weight distribution of Cymel303 polymer

Fig. 2   Molecular weight distribution of Cymel303 grafted with 3hydroxy2 naphthoic acid
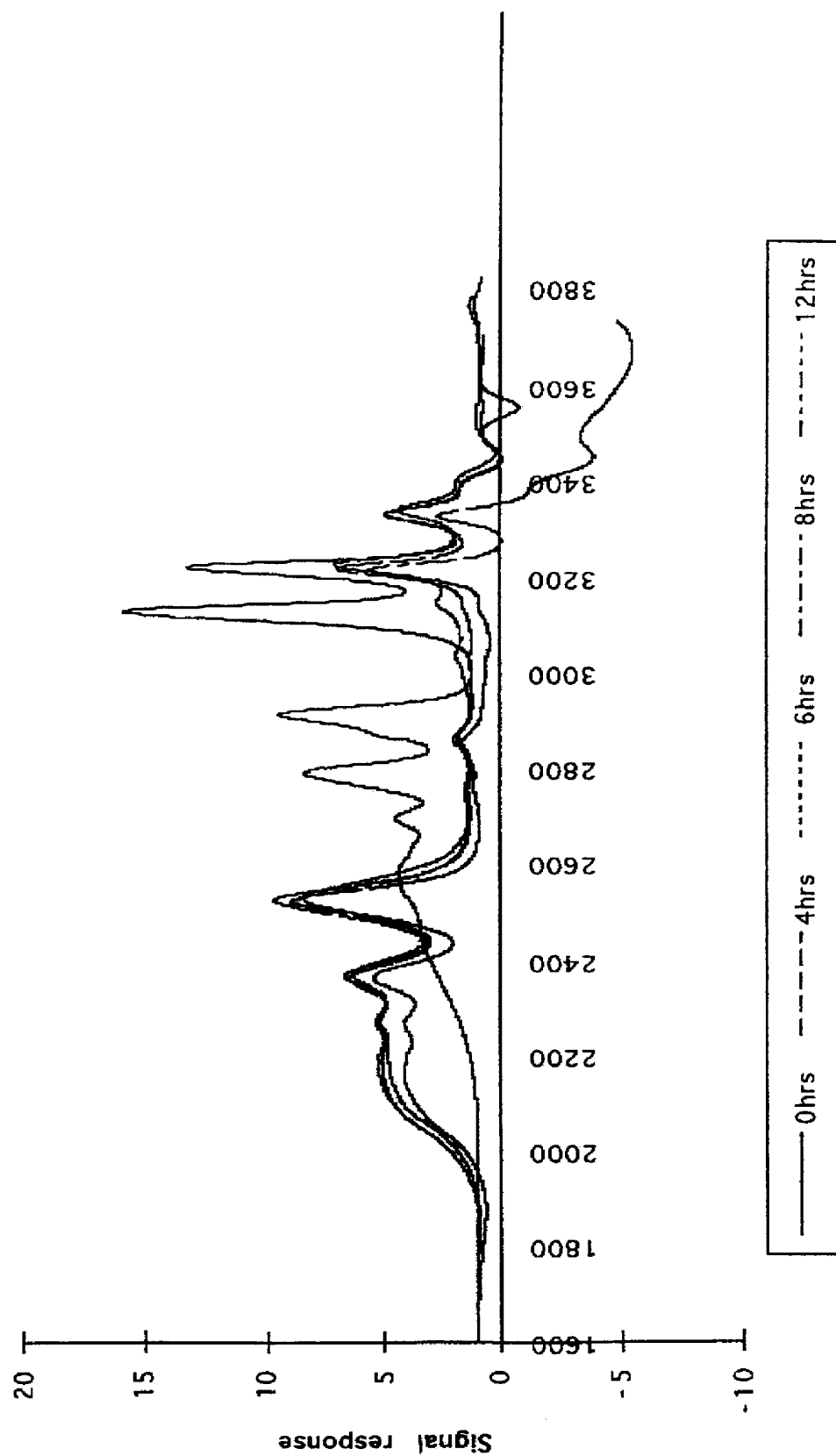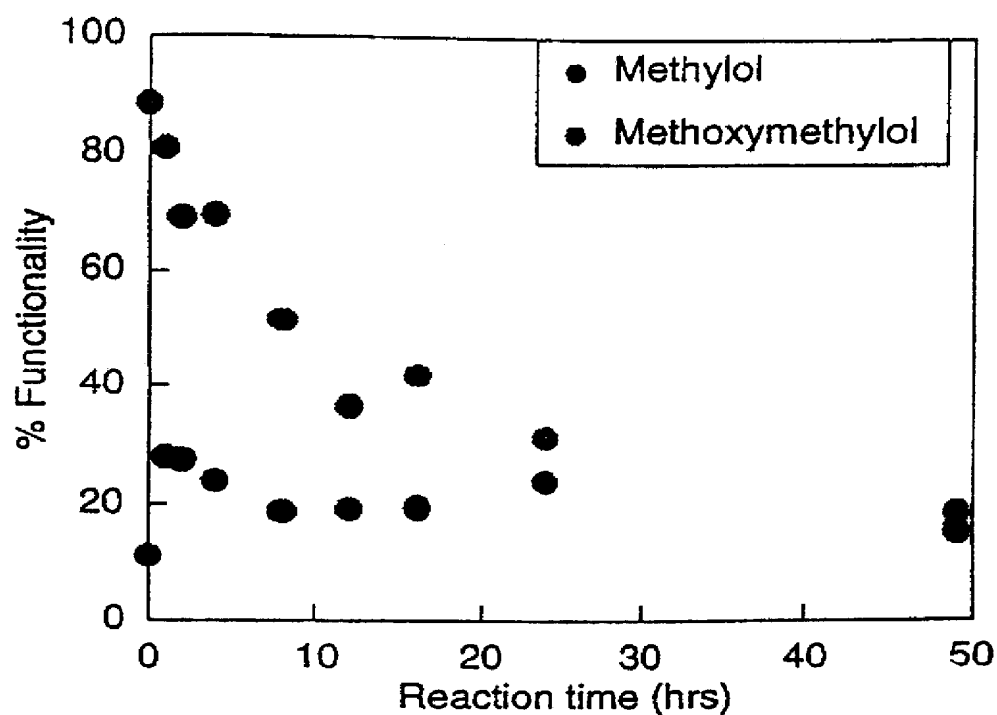
Fig. 3   Time conversion of functionality in Cymel system

	Methylol	Methoxymethylol
0	11.13	88.86
1	27.98	81.48
2	27.36	69.52
4	23.81	69.77
8	18.56	51.87
12	19.10	36.89
16	19.37	42.07
24	24.14	31.43
49	18 ⁴⁵	15.41

ANTI-REFLECTIVE COATING COMPOSITIONS COMPRISING POLYMERIZED AMINOPLASTS

This application is a divisional of U.S. patent application Ser. No. 09/552,236, filed Apr. 19, 2000, now U.S. Pat. No. 6,323,310, incorporated by reference herein.

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention is broadly concerned with anti-reflective compositions and methods of forming the compositions for use as anti-reflective coating (ARC) layers on substrates during integrated circuit manufacturing processes. More particularly, the inventive compositions are formed by polymerizing aminoplasts (e.g., melamine, benzoguanamine) in an acidic environment under elevated temperatures to yield cross-linkable, UV absorbing, fast etching compositions.

2. Description of the Prior Art

A frequent problem encountered by photoresists during the manufacturing of semiconductor devices is that activating radiation is reflected back into the photoresist by the substrate on which it is supported. Such reflectivity tends to cause blurred patterns which degrade the resolution of the photoresist. Degradation of the image in the processed photoresist is particularly problematic when the substrate is non-planar and/or highly reflective. One approach to address this problem is the use of a bottom anti-reflective coating (BARC) applied to the substrate beneath the photoresist layer.

Fill compositions which have high optical density at the typical exposure wavelengths have been used for some time to form these BARC layers. The BARC compositions typically consist of an organic polymer which provides coating properties and a dye for absorbing light. The dye is either blended into the composition or chemically bonded to the polymer. Thermosetting BARC's contain a cross-linking agent in addition to the polymer and dye. Cross-linking must be initiated, and this is typically accomplished by an acid catalyst present in the composition. As a result of all these ingredients which are required to perform specific and different functions, prior art BARC compositions are fairly complex.

U.S. Pat. No. 5,939,510 to Sato et al. discloses a BARC composition which comprises a UV absorber and a cross-linking agent. The UV absorber is a benzophenone compound or an aromatic azomethine compound having at least one unsubstituted or alkyl-substituted amino group on the aryl groups. The cross-linking agent disclosed by Sato et al. is a melamine compound having at least two methylol groups or alkoxymethyl groups bonded to the nitrogen atoms of the molecule.

The Sato et al. composition suffers from two major drawbacks. First, in the two-component composition disclosed, the Sato et al. composition does not include a polymeric material thus resulting in insufficient coverage on the surfaces and edges of the substrate features. Furthermore, the UV absorber disclosed by Sato et al. is physically mixed with the cross-linking agent rather than chemically bonded to some component of the composition. As a result, the UV absorber will often sublime, and in many cases sublime and diffuse into the subsequently applied photoresist layer.

There is a need for a less complex anti-reflective composition which provides high reflection control and increased

etch rates while minimizing or avoiding intermixing with photoresist layers.

SUMMARY OF THE INVENTION

The present invention overcomes these problems by broadly providing improved anti-reflective compositions which are formed from a minimal number of components (e g. two or less) and which exhibit the properties necessary in an effective BARC composition.

In more detail, anti-reflective compositions according to the invention include polymers comprising monomers derived from compounds of Formula I and mixtures thereof.
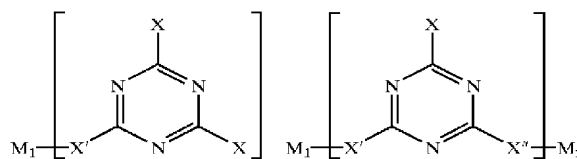
Formula I
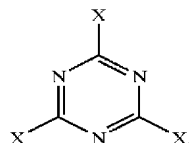
wherein each X is individually selected from the group consisting of NR_2 (with the nitrogen atom being bonded to the ring structure) and phenyl groups, where each R is individually selected from the group consisting of hydrogen, alkoxyalkyl groups, carboxyl groups, and hydroxymethyl groups. Preferred compounds of Formula I include the following:

benzoguanamine   melamine
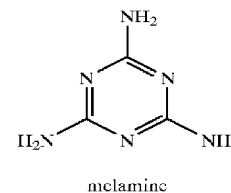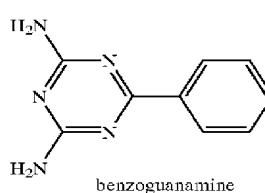
When used in reference to Formula I, the phrase "monomers derived from compounds of Formula I" is intended to refer to functional moieties of Formula I. For example, each of the structures of Formula II is derived from compounds of Formula I.

Formula II

wherein: each X is individually selected from the group consisting of NR_2 (with the nitrogen atom being bonded to the ring structure) and phenyl groups, where each R is individually selected from the group consisting of hydrogen, alkoxyalkyl groups, carboxyl groups, and hydroxymethyl groups; and "M_1" and "M_2" represent a molecule (e.g., a chromophore or another monomer derived from the compound of Formula I) bonded to X' or X". Thus, "monomers derived from the compounds of Formula I" would include those compounds where any of the constituents (i.e., any of the X groups, and preferably 1–2 of the X groups) is bonded to another molecule.

The polymerized monomers are preferably joined by linkage groups selected from the group consisting of

—CH_2—, —CH_2—O—CH_2, and mixtures thereof, with the linkage groups being bonded to nitrogen atoms on the respective monomers. For example, Formula III demonstrates two methoxymethylated melamine moieties joined via a —CH_2— linkage group and two methoxymethylated melamine moieties joined via a —CH_2—O —CH_2— linkage group.

dispersant. Furthermore, the heating step should be carried out for at least about 2 hours, and preferably from about 4–6 hours. In applications where only benzoguanamine-based moieties are utilized, the heating step should be carried out for a time period of less than about 7 hours, and preferably from about 5.5–6.5 hours.

Formula III
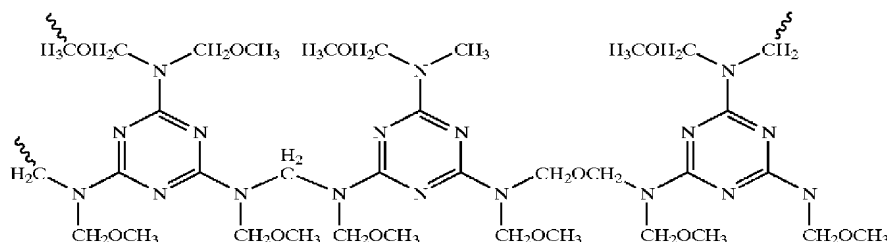
Formula IV illustrates two benzoguanamine moieties joined via CH_2 linkage groups.

Formula IV
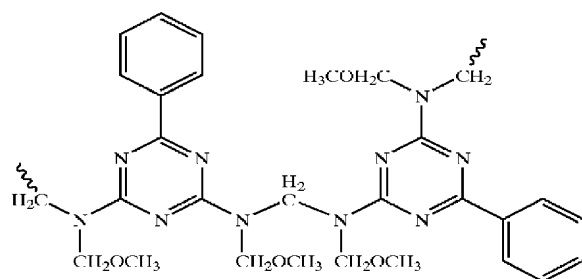
Finally, Formula V illustrates two methoxymethylated melamine moieties having a chromophore (2,4-hexadienoic acid) bonded thereto and joined via CH_2 linkage groups.

Heating the starting compounds under acidic conditions causes the compounds to polymerize by forming the previously described linkage groups. The polymers resulting from the heating step should have an average molecular weight of at least about 1,000 Daltons, preferably at least about 5,000 Daltons, and more preferably at least about 5,000–20,000 Daltons. Furthermore, about 12 hours after the heating step the resulting anti-reflective composition should have a decrease of at least about 20%, preferably at least about 40%, and more preferably from about 40–70% in methoxymethylol (—CH_2OCH_3) groups than were present in the starting dispersions of Formula I compounds, with the quantity of methoxymethylol groups being determined by the titration procedure as herein defined.

It will be appreciated that the inventive polymer compositions provide significant advantages over prior art compositions in that the polymerized compositions alone act as conventional anti-reflective coating polymer binders, cross-linking agents, and chromophores, thus greatly simplifying the anti-reflective coating system.

In applications where enhanced light absorbance is desired, a chromophore (e.g., 2,4-hexadienoic acid,

Formula V

The inventive compositions are formed by providing a dispersion of the compounds of Formula I in a dispersant (preferably an organic solvent such as ethyl lactate), and adding an acid (such as p-toluenesulfonic acid) to the dispersion either prior to or simultaneous to heating of the dispersion to a temperature of at least about 70° C., and preferably at least about 120° C. The quantity of acid added should be from about 0.001–1 moles per liter of dispersant, and preferably from about 0.01–0.5 moles of acid per liter of

3-hydroxy-2-naphthoic acid) can be mixed with the starting dispersion prior to acid and heat treatment. During subsequent acid treatment, the chromophore will chemically bond to the monomers during polymerization.

The resulting polymerized composition is mixed with a solvent to form an anti-reflective coating composition. Suitable solvents include propylene glycol monomethyl ether, propylene glycol monomethyl ether acetate, ethyl lactate, and cyclohexanone. The anti-reflective coating composition

is subsequently applied to the surface of a substrate (e.g., silicon wafer) by conventional methods, such as by spin-coating, to form an anti-reflective coating layer on the substrate. The substrate and layer combination is baked at temperatures of at least about 160° C. The baked layer will generally have a thickness of anywhere from about 500 Å to about 2000 Å.

In an alternate embodiment, an anti-reflective composition is formed by preparing a dispersion including, in a dispersant (e.g., propylene glycol monomethyl ether, pro-pylene glycol monomethyl ether acetate, ethyl lactate), a quantity of the compound of Formula I and a polymer having cross-linking sites therein. The composition should comprise at least about 1.5% by weight of the polymer, and preferably from about 2.0–20% by weight of the polymer, based upon the total weight of the solids in the composition taken as 100% by weight. The molecular weight of the polymer is at least about 2,000 Daltons, and preferably from about 5,000–100,000 Daltons. The cross-linking sites on the polymer preferably comprise a cross-linking group selected from the group consisting of hydroxyl, carboxylic, and amide groups. The most preferred polymers include cellu-lose acetate hydrogen phthalate, cellulose acetate butyrate, hydroxypropyl cellulose, ethyl cellulose, polyesters, poly-acrylic acid, and hydroxypropyl methacrylate.

In this embodiment, it is not necessary to heat the dis-persion. However, as was the case with the first embodiment, the composition preferably includes an acid such as p-toluenesulfonic acid. Advantageously, it is not necessary to add a chromophore to the composition as the compound of Formula I also functions as a light-absorber.

Thus, the composition is preferably essentially free (i.e., less than about 0.5% by weight, preferably less than about 0.1% by weight, and more preferably about 0% by weight) of any added chromophores.

In either embodiment, low molecular weight (e.g., less than about 13,000 Daltons) polymeric binders can be uti-lized in the dispersion (after heating and acidification steps in the case of the first embodiment) to assist in forming highly planar layers. Alternately, a high molecular weight polymeric binder (e.g., acrylics, polyester, or cellulosic polymer such as cellulose acetate hydrogen phthalate, hydroxypropyl cellulose, and ethyl cellulose) having a molecular weight of at least about 100,000 Daltons can be mixed with the starting dispersion (also after heating and acidification steps in the case of the first embodiment) to assist in forming conformal layers. This will result in an anti-reflective layer having a percent conformality of at least about 60%, even on topographic surfaces (i.e., surfaces having raised features of 1000 Å or greater and/or having contact or via holes formed therein having hole depths of from about 1000–15,000 Å).

As used herein, percent conformality is defined as:

$$100 \cdot \frac{|\text{(thickness of the film at location } A) - \text{(thickness of the film at location } B)|}{\text{(thickness of the film at location } A),}$$

wherein: "A" is the centerpoint of the top surface of a target feature when the target feature is a raised feature, or the centerpoint of the bottom surface of the target feature when the target feature is a contact or via hole; and "B" is the halfway point between the edge of the target feature and the edge of the feature nearest the target feature. "Feature" and "target feature" is intended to refer to raised features as well as contact or via holes. As also used in this definition, the "edge" of the target feature is intended to refer to the base

of the sidewall forming the target feature when the target feature is a raised feature, or the upper edge of a contact or via hole when the target feature is a recessed feature. Percent planarization is defined as:

$$100 - \% \text{ conformality.}$$

Regardless of the embodiment, anti-reflective layers formed according to the invention will absorb at least about 90%, and preferably at least about 95%, of light at wave-lengths of from about 190–260 nm. Furthermore, the anti-reflective layers have a k value (i.e., the imaginary compo-nent of the complex index of refraction) of at least about 0.2, and preferably at least about 0.5, at the wavelength of interest. Finally, the anti-reflective layers have high etch rates, particularly when melamine is utilized. The etch selectivity to resist will be at least about 1.5, and preferably at least about 2.0 when CF_4 is used as the etchant.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a graph depicting the molecular weight distri-bution of polymerized Cymel® 303 as a function of reaction time;

FIG. 2 is a graph depicting the molecular weight distri-bution of polymerized Cymel® 303 having 3-hydroxy-2-naphthoic acid bonded thereto as a function of reaction time; and

FIG. 3 is a graph depicting the change in the methylol and methoxymethylol groups over time.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The following examples set forth preferred methods in accordance with the invention. It is to be understood, however, that these examples are provided by way of illustration and nothing therein should be taken as a limita-tion upon the overall scope of the invention.

Testing Procedures

1. Stripping Test Procedure

In the following examples, a stripping test was performed to determine the resistance of the experimental anti-reflective coating (ARC) to photoresist solvents. In this procedure, an ARC formulation was spin-coated onto a silicon wafer at a spin speed of 2,500 rpm for 60 seconds and at an acceleration of 20,000 rpm/second. The film was baked on a hotplate at 205° C. for 60 seconds. The ARC film thickness was then measured at multiple points on the wafer using ellipsometry.

Ethyl lactate was puddled onto the silicon wafer for 10 seconds, followed by spin drying at 3,500 rpm for 30 seconds to remove the solvent. The film was then baked on a hotplate at 100° C. for 30 seconds. The ARC film thickness was again measured at multiple points on the wafer using ellipsometry. The amount of stripping was determined to be the difference between the initial and final average film thicknesses, with the uncertainty in the stripping measure-ment being the sum of the two average thickness measure-ment uncertainties.

2. Interlayer Formation Procedure

In the following examples, the degree of intermixing between the sample ARC and the photoresist was deter-mined. In this procedure, an ARC formulation was spin-coated onto a silicon wafer at a spin speed of 2,500 rpm for 60 seconds and at an acceleration of 20,000 rpm/second. The film was baked on a hotplate at 205° C. for 60 seconds. The ARC film thickness was then measured at multiple points on the wafer using ellipsometry.

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A photoresist (UV6, available from Shipley) was spin-coated on top of the ARC film at a spin speed of 3250 rpm for 30 seconds and at an acceleration of 20,000 rpm/second under ambient conditions. The wafer was then baked on a hotplate for 130° C. for 60 seconds and exposed to 20 mJ of exposure energy, after which a post-exposure bake was performed on the wafer at 130° C. for 90 seconds.

The photoresist was developed with Shipley LDD26W developer for 40 seconds. The sample was then rinsed with distilled water and spun dry at 2,000 rpm for 20 seconds followed by baking on a hotplate for 100° C. for 30 seconds. The film again measured at multiple points on the wafer using ellipsometry. The difference in the two film thickness averages (Å) was recorded as the interlayer stripping result with the uncertainty in the interlayer measurement being the sum of the two average thickness measurement uncertainties.

3. Titration Procedure

a. Free Formaldehyde Analysis

A 10% Na_2SO_3 (aq) solution was prepared by mixing 50 g of Na_2SO_3 with 450 g of water. A few drops of rosolic acid was added to this solution until it turned red after which 1N HCl (aq) was added to the solution until it turned to a color between pale pink and colorless. The shelf life of the resulting solution is 2–3 days.

The sample to be tested was prepared by mixing 1.5 g of the sample with 10 ml of 1,4-dioxane. Next, 20 g of the previously prepared 10% Na_2SO_3 solution was added to the flask and the flask was agitated with a magnetic stirrer. While stirring, 1N HCl (aq) was titrated into the flask until the solution turned pale pink or colorless. The free formaldehyde was then determined by the following equation:

$$Y=[(A-BL)*(30.03/1000)*100]/W,$$

where "A" is the amount (in ml) of titrated 1N HCl, "BL" is the amount (in ml) titrated for a blank (i.e., 1,4-dioxane only), "W" is the weight of the sample in grams, and "Y" is the weight percent of free formaldehyde in the solution. Thus, the total free formaldehyde weight (X) is:

$$[(total\ solution\ weight\ in\ g)*(Y)]/100.$$

b. —CH_2OH Analysis

In this procedure, 1 g of the sample was mixed with 20 ml of 1,4-dioxane in a beaker followed by sonication for two minutes. The solution was then transferred to a flask, and the beaker was rinsed three times with 10 ml portions of water (for a total of 30 ml), with the rinse water being added to the flask after each rinsing. Next, 25 ml of I_2 (0.1N) and 10 ml of 2N NaOH (aq) were added to the solution, the flask was capped tightly, and the solution was allowed to stand for 10 minutes. The solution was then titrated with 0.1N $Na_2S_2O_3$ (aq) until it turned a purple-brown color. The percent —CH_2OH was then determined according to the following equation:

$$\%\ —CH_2OH=(B-A)*0.1*(1.502/weight\ of\ sample\ in\ g)-X,$$

where "A" is the amount (in ml) titrated for a blank (i.e., 1,4-dioxane only), "B" is the amount (in ml) of titrated 0.1N $Na_2S_2O_3$, and "X" is the total free formaldehyde weight determined as described in part (a) above.

c. —CH_2OCH_3 Analysis

In this procedure, 1 g of the sample was mixed with 20 ml of 1,4-dioxane in a beaker followed by sonication for two minutes. The solution was then transferred to a flask, and the beaker was rinsed three times with 10 ml portions of water

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(for a total of 30 ml), with the rinse water being added to the flask after each rinsing. Next, 20 ml of 2N of H_2SO_4 (aq) was added to the flask and the solution was allowed to stand for 20 minutes at a temperature of 30–35° C. To the solution, 25 ml of I_2 (0.1N) and 25 ml of 2N NaOH (aq) were added, the flask was capped tightly, and the solution was allowed to stand for 15 minutes at room temperature. An additional 20 ml of 2N H_2SO_4 (aq) was mixed with the solution, and the solution was titrated with 0.1N $Na_2S_2O_3$ (aq) until it turned from a purple-brown color to colorless. The percent —CH_2OCH_3 was then determined according to the following equation:

$$\%\ —CH_2OCH_3=(B-A)*0.1*(1.502/weight\ of\ sample\ in\ g)-X,$$

where "A" is the amount (in ml) titrated for a blank (i.e., 1,4-dioxane only), "B" is the amount (in ml) of titrated 0.1N $Na_2S_2O_3$, and "X" is the total free formaldehyde weight determined as described in part (a) above.

Example 1

Cymel® 303 (40.0 g, available from Cytec Industries, Inc., New Jersey) was dissolved in 180.0 g of ethyl lactate in a 500 ml round-bottomed flask. In a 50 ml beaker, 1.0 g of p-toluenesulfonic acid (pTSA) was dissolved in 20 g of ethyl lactate. The round-bottomed flask was fitted with a nitrogen source, a water condenser, and a thermometer, and the contents of the flask heated to 120° C. in an oil bath. The pTSA solution was added to the beaker via an addition funnel. The resulting solution was maintained at a temperature of 120° F. for 12 hours. During this 12-hour time period, 50 g aliquots of the solution were collected at 0 hours, 4 hours, 6 hours, 8 hours, and 12 hours, and labeled as Samples 1–5, respectively.

Each of the samples was cooled and filtered through a 0.1 micron filter. An anti-reflective coating was formulated from the cooled samples 1–5 by adding 73.0 g of propylene glycol monomethyl ether (PGME) to the cooled and filtered samples. The molecular weight distribution profiles of these samples were determined using a gel permeation chromatograph with a refractive index detector and 50 Å, 100 Å, and 500 Å Phenogel (Phenomenex) columns in series. These results are shown in FIG. 1.

Silicon wafers were spin-coated with each of the above formulations at 2500 rpm for 60 seconds followed by drying and baking at 205° C. for 60 seconds. The film thickness was measured, and the optical parameters of the film were determined. This data is reported in Table 1. The etch selectivity to resist (DUV42) with CF_4 as the etchant was 1.52.

TABLE 1

Sample	Reaction time (hours)	Thickness Å	n	k	Stripping Test Å	Interlayer Test Å
1	0	1341	2.08	0.182	−2 ± 11	30 ± 34
2	4	1657	2.07	0.247	−88 ± 41	84 ± 42
3	6	1728	2.08	0.229	−20 ± 17	93 ± 15
4	8	1741	2.07	0.237	−23 ± 21	92 ± 21
5	12	1877	2.07	0.237	−14 ± 13	101 ± 38

Example 2

Cymel® 303 (40.0 g) and 8.0 g of 3-hydroxy 2-naphthoic acid were dissolved in 180.0 g of ethyl lactate in a 500 ml round-bottomed flask. In a 50 ml beaker, 1.0 g of pTSA was

dissolved in 20 g of ethyl lactate. The round-bottomed flask was fitted with a nitrogen source, a water condenser, and a thermometer, and the contents of the flask heated to 120° C. in an oil bath. The pTSA solution was added to the beaker via an addition funnel. The resulting solution was maintained at a temperature of 120° F. for 12 hours. During this 12-hour time period, 50 g aliquots of the solution were collected at 0 hours, 4 hours, 6 hours, 8 hours, and 12 hours, and labeled as Samples 1–5, respectively.

Each of the samples was cooled and filtered through a 0.1 micron filter. An anti-reflective coating was formulated from samples 1–5 by adding 73.0 g of PGME to the cooled and filtered samples. The molecular weight distribution profiles of these samples were determined using a gel permeation chromatograph with a refractive index detector and 50 Å, 100 Å, and 500 Å Phenogel columns in series. These results are shown in FIG. 2.

Silicon wafers were spin-coated with each of the above formulations at 2500 rpm for 60 seconds followed by drying and baking at 205° C. for 60 seconds. The film thickness was measured, and the optical parameters of the film were determined. This data is reported in Table 2. The etch selectivity to resist (DUV42) with CF_4 as the etchant was 1.40.

TABLE 2

Sample	Reaction time (hours)	Thickness Å	n	k	Stripping Test Å	Interlayer Test Å
1	0	2255	2.08	0.477	−4 ± 17	40 ± 64
2	4	2021	2.07	0.459	2 ± 17	61 ± 27
3	6	1928	2.08	0.469	−2 ± 8	61 ± 34
4	8	1926	2.08	0.468	−7.8 ± 13	63 ± 11
5	12	1957	2.07	0.461	8.8 ± 0	50 ± 49

Example 3

Cymel® 303 and Cymel® 1123 (see Table 3 for amounts) were dissolved along with 0.75 g of pTSA were dissolved in 150.0 g of ethyl lactate in a 500 ml round-bottomed flask. The flask was fitted with a nitrogen source, a water condenser, and a thermometer after which the flask contents were heated to 120° C. in an oil bath and maintained at this temperature for 12 hours. The sample was filtered through a 0.1 micron filter. An anti-reflective coating was formulated by adding PGME, p-toluenesulfonate or pyridine, and pyridinium tosylate (pPTS) to the prepared sample in the amounts indicated in Table 3.

The formulations were spin-coated on silicon wafers at 2500 rpm for 60 seconds followed by drying and baking at 205° C. for 60 seconds. The respective thicknesses of the films were measured, and the optical parameters were determined. This data is reported in Table 4.

TABLE 3

Formulation	Cymel ® 303	Cymel ® 1123	PGME	Total Ethyl lactate	pyridine	pPTS	Total pTSA
I	10 g	20 g	336.2 g	247.6 g	—	—	2 g
II	25 g	5 g	336.3 g	247.6 g	—	—	2 g
III	10 g	20 g	336.2 g	247.6 g	0.3 g	1.65 g	0.75 g
IV	25 g	5 g	336.2 g	247.6 g	0.3 g	1.65 g	0.75 g

TABLE 4

Formulation	Thickness Å	n	k	Stripping Test Å	Interlayer Test Å	Etch Selectivity[A]
I	749	1.970	0.484	−2	39	1.3
II	720	2.106	0.363	0	30	1.6
III	747	1.945	0.461	2	40	1.3
IV	740	2.096	0.358	0	20	1.6

[A]Selectivity to resist (DUV42) with CF_4 as the etchant.

Example 4

Cellulose acetate hydrogen phthalate (3.0 g and having an average molecular weight of about 100,000 Daltons) was dissolved in 130.5 g of PGME. Next, 11.5 g of Cymel® 1125, 5.0 g of Cymel® 303, 150 g of propylene glycol monomethyl ether acetate (PGMEA), and 1.15 g of pTSA was added to the prepared solution and allowed to dissolve completely. The resulting solution was then filtered through a 0.1 micron.

The prepared formulation was spin-coated on silicon wafers at 2500 rpm for 60 seconds followed by drying and baking at 205° C. for 60 seconds. The film thickness was measured, and the optical properties determined. This data is reported in Table 5. The percent conformality of the film was determined to be 60%.

TABLE 5

| Thickness Å	n	k	Stripping Test Å	Interlayer Test Å
1280	1.92	0.35	0 ± 10	0 ± 40

Example 5

Cymel® 303 (25 g) and Cymel® 1123 (5 g) were dissolved along with 2 g of pTSA in 247.6 g of ethyl lactate. The resulting mixture was heated to 120° C., and the methylol and methoxymethylol groups were measured over time according to above-defined titration procedure. These results are shown in FIG. 3. As indicated by these results, the methoxymethylol groups decreased over time as the Cymel® polymerized. It is believed that the methylol groups may be regenerating or that new methylol groups are forming during polymerization since the methoxymethylol groups are involved in the polymerization.

What is claimed is:

1. A method of preparing a polymer composition, said method comprising the steps of:

providing a dispersion including a quantity of a compound according to the formula:
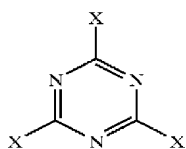
wherein each X is individually selected from the group
consisting of NR$_2$ and phenyl groups, where each R
is individually selected from the group consisting of
hydrogen, alkoxyalkyl groups, carboxyl groups, and
hydroxymethyl groups;

adding to said dispersion from about 0.001–1 moles of an
acid per liter of said dispersion; and

heating said dispersion to a temperature of at least about
70° C. for at least about 2 hours to yield the polymer
composition.

2. The method of claim 1, wherein said acid addition step
comprises adding p-toluenesulfonic acid to said dispersion.

3. The method of claim 1, wherein said acid addition step
and said heating step are carried out substantially simulta-
neously.

4. The method of claim 1, wherein said heating step is
carried out after said acid addition step.

5. The method of claim 1, wherein the polymer compo-
sition resulting from said heating step comprises polymers
having an average molecular weight of at least about 1,000
Daltons.

6. The method of claim 1, wherein the compound of said
providing step comprises a plurality of said Formula I
compounds and an initial quantity of methoxymethylol
groups and wherein about 12 hours after commencement of
said heating step, the quantity of methoxymethylol groups
present in the resulting polymer composition decreases by at
least about 20% when compared to said initial quantity, with
the quantity of methoxymethylol groups being determined
by the titration procedure.

7. The method of claim 1, wherein said compound is
selected from the group consisting of benzoguanamine and
melamine.

8. The method of claim 7, wherein said compound is
benzoguanamine and said heating step is carried out for a
time period of less than about 7 hours.

9. The method of claim 1, further including the step of
mixing a chromophore with said dispersion prior to or
during said acid addition step.

10. The method of claim 9, wherein said chromophore is
selected from the group consisting of 2,4-hexadienoic acid
and 3-hydroxy-2-naphthoic acid.

11. The method of claim 9, wherein the polymer compo-
sition resulting from said heating step comprises a polymer,
and said chromophore is chemically bonded to said polymer.

12. The method of claim 1, wherein the polymer compo-
sition resulting from said heating step comprises polymers
which comprise recurring monomers of said compound, said
recurring monomers being joined together by linkage groups
selected from the group consisting of —CH$_2$—, —CH$_2$—
O—CH$_2$—, and mixtures thereof.

13. The method of claim 1, wherein the polymer compo-
sition resulting from said heating step comprises polymers
which comprise recurring monomers of said compound, said
recurring monomers being joined together by linkage groups
which bond to nitrogen atoms on the respective compounds.

14. A method of preparing a composition, said method
comprising the step of forming a dispersion including, in a
dispersant:

a quantity of a compound according to the formula:
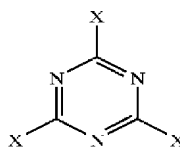
wherein each X is individually selected from the group
consisting of NR$_2$ and phenyl groups, where each R
is individually selected from the group consisting of
hydrogen, alkoxyalkyl groups, carboxyl groups, and
hydroxymethyl groups; and

a polymer having cross-linking sites therein to yield the
composition, said polymer being present in said com-
position at a level of from about 2.0–20% by weight,
based upon the total weight of the solids in the com-
position taken as 100% by weight.

15. The method of claim 14, wherein said forming steps
comprises adding an acid to said dispersion.

16. The method of claim 14, wherein said acid comprises
p-toluenesulfonic acid.

17. The method of claim 14, wherein said dispersant is a
solvent selected from the group consisting of propylene
glycol monomethyl ether, propylene glycol monomethyl
ether acetate, and ethyl lactate.

*   *   *   *   *

US006503689B2

(12) **United States Patent** (10) Patent No.: **US 6,503,689 B2**
Zampini et al. (45) **Date of Patent:** **Jan. 7, 2003**

(54) **ANTIREFLECTIVE COMPOSITION**

(75) Inventors: **Anthony Zampini**, Westborough, MA (US); **Manuel Docanto**, Stoughton, MA (US); **Robert H. Gore**, Southampton, PA (US)

(73) Assignee: **Shipley Company, L.L.C.**, Marlborough, MA (US)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

(21) Appl. No.: **09/956,531**

(22) Filed: **Sep. 19, 2001**

(65) **Prior Publication Data**

US 2002/0076642 A1 Jun. 20, 2002

Related U.S. Application Data

(60) Provisional application No. 60/233,517, filed on Sep. 19, 2000.

(51) Int. Cl.^{7} **G03F 7/004**
(52) U.S. Cl. **430/270.1**; 430/510; 430/325; 430/311; 430/271.1; 428/327

(58) Field of Search 430/270.1, 271.1, 430/325, 311, 510; 428/327

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Primary Examiner—Rosemary Ashton
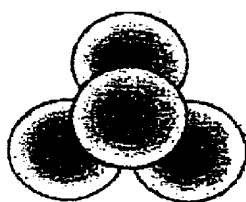(74) *Attorney, Agent, or Firm*—S. Matthew Cairns

(57) **ABSTRACT**

Disclosed are new antireflective compositions including cross-linked polymeric particles including one or more chromophores. Also disclosed are methods of forming relief images using these antireflective compositions.
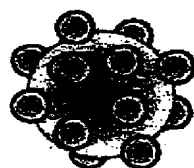
28 Claims, 4 Drawing Sheets
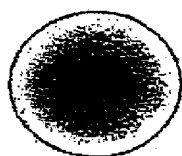
Fig. 1

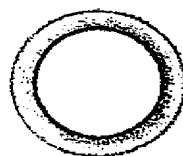Polymer Particle Morphology and Structure
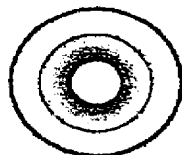

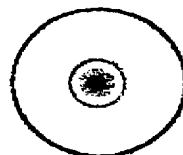tetrahedral   raspberry

Multilobes

Structure

Uniform   **Egg-Shell**

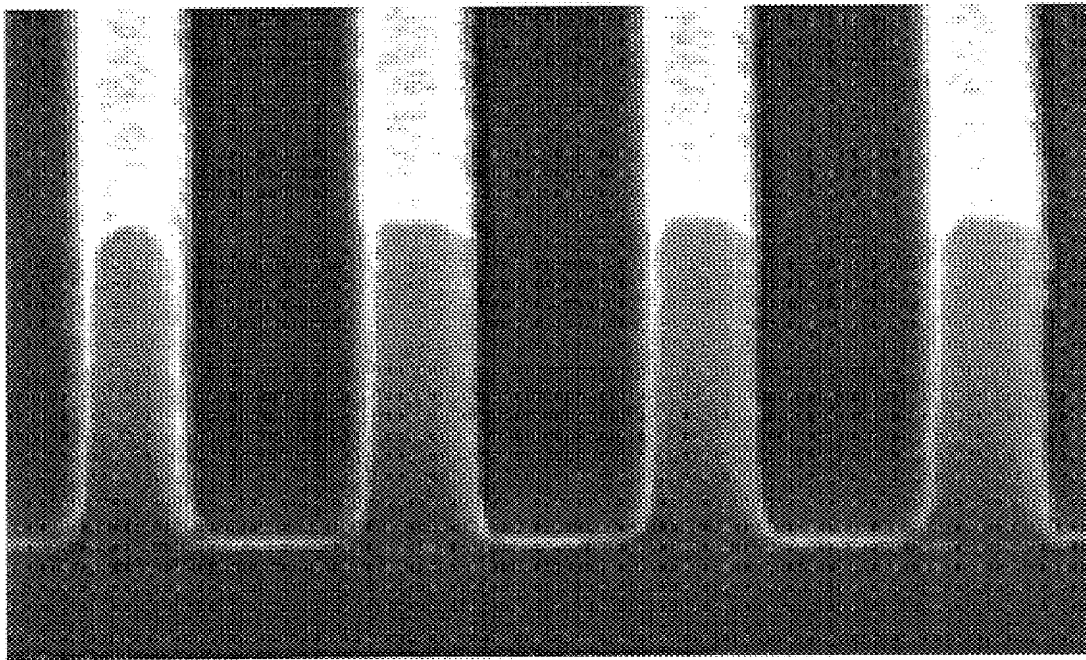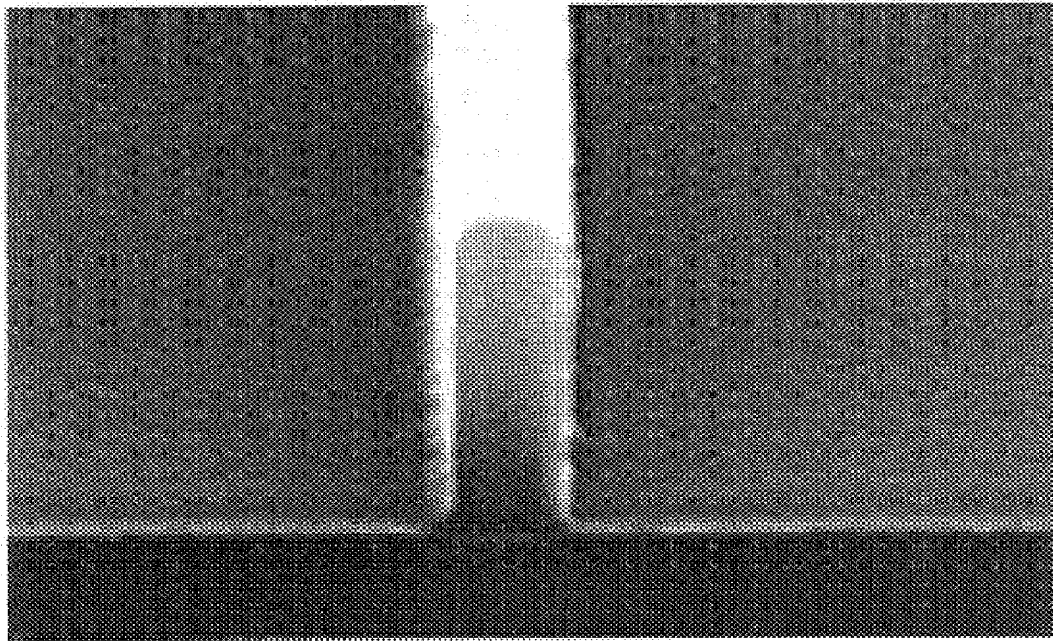**Egg-White**   **Egg-Yolk**
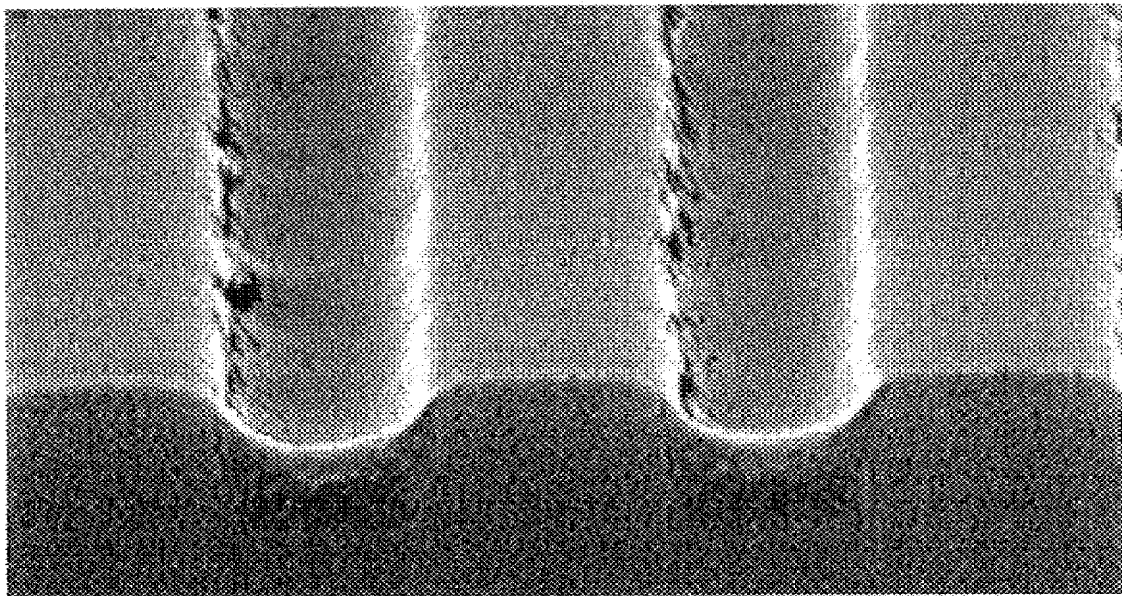
Fig. 2

Fig. 3

Fig. 4

ANTIREFLECTIVE COMPOSITION

This application claims the benefit of Ser. No. 60/233,517, filed Sep. 19, 2000.

BACKGROUND OF THE INVENTION

The present invention relates generally to the field of antireflective compositions. In particular, the present invention relates to polymer compositions useful in antireflective compositions.

In the manufacture of electronic devices, such as printed wiring boards or semiconductors, a number of layers of material, such as photoresists or antireflective coatings, are applied to a substrate. Photoresists are photosensitive films used for transfer of an image to a substrate. A coating layer of a photoresist is formed on a substrate and the photoresist layer is then exposed through a photomask (reticle) to a source of activating radiation. The photomask has areas that are opaque to activating radiation and other areas that are transparent to activating radiation. Exposure to activating radiation provides a photoinduced chemical transformation of the photoresist coating to thereby transfer the pattern of the photomask to the photoresist coated substrate. Following exposure, the photoresist is developed to provide a relief image that permits selective processing of a substrate.

A photoresist can be either positive-acting or negative-acting. For most negative-acting photoresists, those coating layer portions that are exposed to activating radiation polymerize or cross-link in a reaction between a photoactive compound and polymerizable reagents of the photoresist composition. Consequently, the exposed coating portions are rendered less soluble in a developer solution than unexposed portions. For a positive-acting photoresist, exposed portions are rendered more soluble in a developer solution while areas not exposed remain comparatively less developer soluble. Photoresist compositions are known to the art and described by Deforest, Photoresist Materials and Processes, McGraw Hill Book Company, New York, ch. 2, 1975 and by Moreau, Semiconductor Lithography, Principles, Practices and Materials, Plenum Press, New York, ch. 2 and 4, both incorporated herein by reference to the extent they teach photoresist compositions and methods of making and using them.

A major use of photoresists is in the manufacture of semiconductors where an object is to create features, such as vias, trenches or combinations thereof, in a dielectric layer. Proper photoresist processing is a key to attaining this object. While there is a strong interdependency among the various photoresist processing steps, exposure is believed to be one of the more important steps in attaining high resolution photoresist images.

In such processes, reflection of actinic radiation during exposure of the photoresist is detrimental to fine feature formation. Reflection of actinic radiation, such as from the layer underlying the photoresist, often poses limits on resolution of the image patterned in the photoresist layer. Reflection of radiation from the substrate/photoresist interface can produce variations in the radiation intensity in the photoresist during exposure, resulting in non-uniform photoresist linewidth upon development. Radiation also can scatter from the substrate/photoresist interface into regions of the photoresist where exposure is not intended, again resulting in linewidth variations. The amount of scattering and reflection will typically vary from region to region, resulting in further linewidth non-uniformity.

Reflection of activating radiation also contributes to what is known in the art as the "standing wave effect." To eliminate the effects of chromatic aberration in exposure equipment lenses, monochromatic or quasi-monochromatic radiation is commonly used in photoresist projection techniques. Due to radiation reflection at the photoresist/substrate interface, however, constructive and destructive interference is particularly significant when monochromatic or quasi-monochromatic radiation is used for photoresist exposure. In such cases the reflected light interferes with the incident light to form standing waves within the photoresist. In the case of highly reflective substrate regions, the problem is exacerbated since large amplitude standing waves create thin layers of underexposed photoresist at the wave minima. The underexposed layers can prevent complete photoresist development causing edge acuity problems in the photoresist profile. The time required to expose the photoresist is generally an increasing function of photoresist thickness because of the increased total amount of radiation required to expose an increased amount of photoresist. However, because of the standing wave effect, the time of exposure also includes a harmonic component which varies between successive maximum and minimum values with the photoresist thickness. If the photoresist thickness is non-uniform, the problem becomes more severe, resulting in variable linewidths.

With recent trends towards high-density semiconductor devices, there is a movement in the industry to shorten the wavelength of exposure sources to deep ultraviolet (DUV) light (300 nm or less in wavelength), KrF excimer laser light (248 nm), ArF excimer laser light (193 nm), electron beams and soft x-rays. The use of shortened wavelengths of light for imaging a photoresist coating has generally resulted in increased reflection from the upper resist surface as well as the surface of the underlying substrate. Thus, the use of the shorter wavelengths has exacerbated the problems of reflection from a substrate surface.

Radiation reflection problems have been addressed by the addition of certain dyes to photoresist compositions, the dyes absorbing radiation at or near the wavelength used to expose the photoresist. Such dyes have included the coumarin family, methyl orange and methanil yellow. However, the use of such dyes can limit resolution of the patterned resist image.

Another approach used to reduce the problem of reflected radiation has been the use of a radiation absorbing layer either interposed between the substrate surface and the photoresist coating layer, called a bottom antireflective coating or BARC, or a radiation layer disposed on the surface of the photoresist layer, called a top antireflective coating or TARC. See, for example, PCT Application WO 90/03598, EPO Application No. 0 639 941 A1 and U.S. Pat. Nos. 4,910,122, 4,370,405 and 4,362,809, all incorporated herein by reference to the extent they teach antireflective (antihalation) compositions and the use of the same. Such BARC and TARC layers have also been generally referred to in the literature as antireflective layers or antireflective compositions. Typically, such antireflective compositions include a radiation absorbing component (or chromophore) a polymeric binder and one or more cross-linking agents. For example, conventional antireflective compositions typically include an epoxy-phenol binder having no free hydroxyl groups or an acrylate binder substantially free of acid groups.

Variations in substrate topography also give rise to resolution-limiting reflection problems. Any image on a substrate can cause impinging radiation to scatter or reflect in various uncontrolled directions, affecting the uniformity of photoresist development. As substrate topography

becomes more complex with efforts to design more complex circuits, the effects of reflected radiation become more critical. For example, metal interconnects used on many microelectronic substrates are particularly problematic due to their topography and regions of high reflectivity.

One method of solving such problems resulting from variations in substrate topography is by placing a photoresist at the same height over a surface, as disclosed in U.S. Pat. No. 4,557,797 (Fuller et al.). This patent uses a multi-layer structure having a relatively thick bottom layer of poly (methyl methacrylate) ("PMMA") to provide a planar surface, a thin middle layer of an antireflective coating and a thin top layer of a photoresist material. However, this system results in a thick polymer layer which must subsequently be removed. Such layers are typically removed by a variety of methods, such as chemical mechanical polishing ("CMP"), etching and wet chemical methods. Due to the added time and cost of such removal processes, it is desired that the polymer layers be as thin as possible to aid in their subsequent removal.

Another approach to solving the problems associated with variations in substrate topography is that disclosed in Adams et al., *Planarizing AR for DUV Lithography, Microlithography* 1999: *Advances in Resist Technology and Processing XVI*, Proceedings of SPIE, vol. 3678, part 2, pp 849–856, 1999, which discloses the use of a planarizing antireflective coating, which reduces the need for a separate planarizing layer disposed between the antireflective layer and the substrate.

Current antireflective coating compositions include one or more polymeric binders, and optionally a cross-linking agent. The polymeric binders are typically linear polymers having relatively low molecular weights, such as up to 20,000 Daltons. Such polymeric binders are desired as they tend to form coatings of uniform thickness, form planarized coating layers and can be easily dispensed onto a substrate for lithographic processing. The etch rates of antireflective coatings should be equal to or faster than the etch rate of the photoresist used in order to prevent undercutting. However, it is often difficult to substantially match the etch rates of the antireflective coating material to the photoresist while still providing a sufficiently absorbing coating.

Other forms of polymeric binders, such as polymer particles, have not been used as binders in antireflectant compositions. Such polymer particles have a number of advantages over linear polymers, including better control of etch rates, fewer cross-linking events needed, the ability to incorporate multiple absorbing components, and better molecular weight distribution. However, such polymer particles have been thought difficult to dispense to provide a uniform coating on a substrate, that they would not provide sufficiently planar coatings and that they are highly prone to defects.

Thus, there is a continuing need for antireflectant materials that are planarizing and have better etch rate match with the photoresist employed.

SUMMARY OF THE INVENTION

It has been surprisingly found that polymeric particles are effective as antireflective compositions. It has also been surprisingly found that the etch rates of such polymeric particles can be controlled so as to substantially match or exceed that of the photoresist employed. Also, the antireflective compositions of the present invention have lower viscosity than conventional antireflective compositions and thus provide coatings having better planarization. The

present polymeric particles can also be taken up in a greater variety of solvents than conventional antireflective compositions, thus providing greater flexibility in the application of the present compositions to substrates. The present compositions are particularly useful as antireflective coatings for sub-300 nm wavelength exposure, and more particularly for 248 nm, 193 nm and 157 nm wavelengths.

In one aspect, the present invention provides an antireflective composition including a plurality of cross-linked polymeric particles having one or more chromophores.

In a second aspect, the present invention provides a method for forming an antireflective coating layer including the step of disposing on a substrate a composition including a plurality of cross-linked polymeric particles having one or more chromophores.

In a third aspect, the present invention provides a method for forming a photoresist relief image, including the steps of applying a coating layer of an antireflective composition including a plurality of cross-linked polymeric particles having one or more chromophores; applying a photoresist coating layer to the surface of the antireflective coating layer; exposing the photoresist coating layer to patterned activating radiation; and developing the exposed photoresist coating layer to provide a photoresist relief image.

In a fourth aspect, the present invention provides an antireflective composition including a plurality of cross-linked core-shell polymeric particles having one or more chromophores, wherein an absorbing component is contained within the polymeric particle.

In a fifth aspect, the present invention provides a method for manufacturing an electronic device including the steps of disposing on the surface of a substrate a coating layer of an antireflective composition including a plurality of cross-linked polymer particles having one or more chromophores; disposing on the surface of the antireflective coating layer a coating layer of a photoresist composition; exposing the photoresist coating layer to patterned activating radiation; and developing the exposed photoresist coating layer to provide a photoresist relief image.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 illustrates a variety of polymer particle morphologies and structures useful in the present invention.

FIG. 2 is a scanning electron micrograph of 220 nm nested features imaged using the antireflective compositions of the present invention.

FIG. 3 is a scanning electron micrograph of a 220 nm isolated feature imaged using the antireflective compositions of the present invention.

FIG. 4 is a scanning electron micrograph showing planarization of the antireflective compositions of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

As used throughout this specification, the following abbreviations shall have the following meanings, unless the context clearly indicates otherwise: °C.=degrees Centigrade; w/w=weight per weight basis; Å=angstrom; nm=nanometer; t-BMA=tert-butyl methacrylate; MMA=methyl methacrylate; TMPTMA=trimethylolpropane trimethacrylate; TFE= tetrafluoroethylene; and ANTMA=anthracenyl methacrylate.

The terms "resin" and "polymer" are used interchangeably throughout this specification. The term "alkyl" refers to

linear, branched and cyclic alkyl. The terms "halogen" and "halo" include fluorine, chlorine, bromine, and iodine. Thus the term "halogenated" refers to fluorinated, chlorinated, brominated, and iodinated. "Fluoroalkyl" refers to both partially fluorinated and perfluorinated alkyl. "Polymers" refer to both homopolymers and copolymers and include dimers, trimers, oligomers and the like. The term "(meth) acrylate" refers to both acrylate and methacrylate. Likewise, the term "(meth)acrylic" refers to both acrylic and meth-acrylic. "Monomer" refers to any ethylenically or acetyleni-cally unsaturated compound capable of being polymerized. The terms "cross-linker" and "cross-linking agent" are used interchangeably throughout this specification. "Antireflec-tant" and "antireflective" are used interchangeably through-out this specification. As used herein, "chromophore" refers to any radiation absorbing moiety or compound.

All amounts are percent by weight and all ratios are by weight, unless otherwise noted. All numerical ranges are inclusive and combinable.
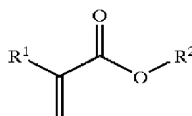
The antireflective compositions of the present invention include one or more cross-linked polymeric particles having one or more chromophores. Preferably, the antireflective compositions further include one or more cross-linking agents and one or more cross-linking catalysts. "Polymer particles" or "polymeric particles" are well known to those skilled in the art and refer to a wide variety of hyperbranched polymeric materials, such as, but not limited to, particles, nanoparticles, nanogels, core-shell particles, and the like. Preferred polymeric particles are nanoparticles and nano-gels. The polymeric particles may have a variety of morphologies, including single-lobed such as spherical, sub-stantially spherical, cigar-shaped, rod-shaped and moon-shaped, and multilobed such as tetrahedral, raspberry, acorn, dumb-bell and the like. The particles useful in the present invention may also have a variety of structures such as uniform or core-shell such as egg-shell, egg-white and egg-yolk. FIG. 1 illustrates a variety of possible polymer particle morphologies and structures. It is preferred that the particles are single-lobed. As used herein, "polymer par-ticles" do not include linear polymers or dendrimer poly-mers.

A wide variety of polymeric particles may be used in the present invention. Such polymeric particles may be homopolymers or copolymers, and preferably are copoly-mers. Thus, the polymeric particles useful in the present invention include as polymerized units one or more ethyl-enically or acetylenically unsaturated monomers. Preferably, the polymeric particles include as polymerized units one or more monomers including a chromophore. As used herein, "chromophore" refers to a group that absorbs and/or attenu-ates the desired wavelength of the radiation used to image the photoresist. For example, when the antireflective coating compositions of the present invention are to be used with photoresists for imaging at radiation wavelengths such as 248 or 193 nm, any monomers containing as the chro-mophore aromatic or substituted aromatic moieties may be used. Such aromatic monomers may be used to form the uncross-linked polymer, used as the cross-linker or both. Suitable aromatic monomers include, but are not limited to, those containing phenyl, substituted phenyl, naphthyl, sub-stituted naphthyl, anthracenyl, substituted anthracenyl, phenanthrenyl, substituted phenanthrenyl, and the like. "Substituted aromatic" refers to aromatic groups having one or more of their hydrogens replaced with one or more other substituent groups, such as (C_1-C_{12})alkyl, halo, cyano, (C_1-C_6)alkoxy, and the like. Suitable anthracenyl mono-mers are disclosed in U.S. Pat. No. 5,851,730 (Thackery et
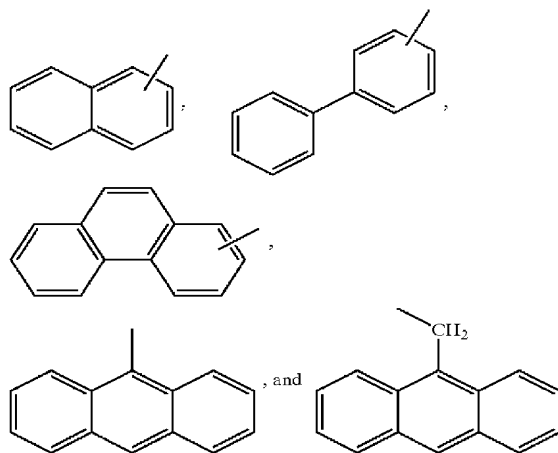
al.). Particularly useful chromophore containing monomers are those of formula I

(I)

wherein R^1 is H or CH_3; and R^2 is selected from phenyl, benzyl,

When the antireflective coating compositions of the present invention are to be used with photoresists for imag-ing at short wavelengths such as 157 nm or below, any monomer containing one or more (C_4-C_{20})alkyl groups is suitable as the chromophore. Particularly useful chro-mophore containing monomers include (C_4-C_{20})alkyl (meth)acrylates such as butyl(meth)acrylate, hexyl(meth) acrylate, octyl(meth)acrylate, nonyl(meth)acrylate, decyl (meth)acrylate, dodecyl(meth)acrylate, hexadecyl(meth) acrylate, octadecyl(meth)acrylate and the like.

It will be appreciated by those skilled in the art that the absorption or attenuation of the antireflective compositions of the present invention may be increased by increasing the amount of such chromophores in the polymeric particles.

It will be appreciated by those skilled in the art that one or more ethylenically unsaturated monomers, acetylenically unsaturated monomers or mixtures thereof may be copoly-merized with the one or more monomers including chro-mophores. Such ethylenically or acetylenically unsaturated monomers or mixtures thereof may be present in the poly-mers of the present invention in an amount in the range of 1 to 99 percent by weight, based on the total weight of the monomers, preferably from 10 to 95 percent by weight, more preferably from 20 to 90 percent by weight, and even more preferably from 60 to 90 percent by weight. It is further preferred that the polymeric particles are crosslinked. Pre-ferred polymeric particles contain as polymerized units, one or more monomers including a chromophore, one or more additional monomers and one or more cross-linking agents.

The one or more additional ethylenically or acetylenically unsaturated monomers that may be copolymerized in the present invention include, but are not limited to: (meth) acrylic acid, (meth)acrylamides, alkyl(meth)acrylates, alkenyl(meth)acrylates, aromatic(meth)acrylates, vinyl aro-matic monomers, nitrogen-containing compounds and their

thio-analogs, substituted ethylene monomers, cyclic olefins, substituted cyclic olefins, and the like.

Typically, the alkyl(meth)acrylates useful in the present invention are (C_1-C_{24})alkyl(meth)acrylates. Suitable alkyl (meth)acrylates include, but are not limited to, "low cut" alkyl(meth)acrylates, "mid cut" alkyl(meth)acrylates and "high cut" alkyl(meth)acrylates. "Low cut" alkyl(meth) acrylates are typically those where the alkyl group contains from 1 to 6 carbon atoms. Suitable low cut alkyl(meth) acrylates include, but are not limited to: methyl methacrylate ("MMA"), methyl acrylate, ethyl acrylate, propyl methacrylate, butyl methacrylate ("BMA"), butyl acrylate ("BA"), isobutyl methacrylate ("IBMA"), hexyl methacrylate, cyclohexyl methacrylate, cyclohexyl acrylate and mixtures thereof.

"Mid cut" alkyl(meth)acrylates are typically those where the alkyl group contains from 7 to 15 carbon atoms. Suitable mid cut alkyl(meth)acrylates include, but are not limited to: 2-ethylhexyl acrylate ("EHA"), 2-ethylhexyl methacrylate, octyl methacrylate, decyl methacrylate, isodecyl methacrylate ("IDMA", based on branched (C_{10})alkyl isomer mixture), undecyl methacrylate, dodecyl methacrylate (also known as lauryl methacrylate), tridecyl methacrylate, tetradecyl methacrylate (also known as myristyl methacrylate), pentadecyl methacrylate and mixtures thereof. Particularly useful mixtures include dodecyl-pentadecyl methacrylate ("DPMA"), a mixture of linear and branched isomers of dodecyl, tridecyl, tetradecyl and pentadecyl methacrylates; and lauryl-myristyl methacrylate ("LMA").

"High cut" alkyl(meth)acrylates are typically those where the alkyl group contains from 16 to 24 carbon atoms. Suitable high cut alkyl(meth)acrylates include, but are not limited to: hexadecyl methacrylate, heptadecyl methacrylate, octadecyl methacrylate, nonadecyl methacrylate, cosyl methacrylate, eicosyl methacrylate and mixtures thereof. Particularly useful mixtures of high cut alkyl(meth)acrylates include, but are not limited to: cetyl-eicosyl methacrylate ("CEMA"), which is a mixture of hexadecyl, octadecyl, cosyl and eicosyl methacrylate; and cetyl-stearyl methacrylate ("SMA"), which is a mixture of hexadecyl and octadecyl methacrylate.

The mid-cut and high-cut alkyl(meth)acrylate monomers described above are generally prepared by standard esterification procedures using technical grades of long chain aliphatic alcohols, and these commercially available alcohols are mixtures of alcohols of varying chain lengths containing between 10 and 15 or 16 and 20 carbon atoms in the alkyl group. Examples of these alcohols are the various Ziegler catalyzed ALFOL alcohols from Vista Chemical company, i.e., ALFOL 1618 and ALFOL 1620, Ziegler catalyzed various NEODOL alcohols from Shell Chemical Company, i.e. NEODOL 25L, and naturally derived alcohols such as Proctor & Gamble's TA-1618 and CO-1270. Consequently, for the purposes of this invention, alkyl(meth) acrylate is intended to include not only the individual alkyl(meth)acrylate product named, but also to include mixtures of the alkyl(meth)acrylates with a predominant amount of the particular alkyl(meth)acrylate named.

The alkyl(meth)acrylate monomers useful in the present invention may be a single monomer or a mixture having different numbers of carbon atoms in the alkyl portion. Also, the (meth)acrylamide and alkyl(meth)acrylate monomers useful in the present invention may optionally be substituted. Suitable optionally substituted (meth)acrylamide and alkyl(meth)acrylate monomers include, but are not limited to: hydroxy (C_2-C_6)alkyl(meth)acrylates, dialkylamino (C_2-C_6)-alkyl(meth)acrylates, dialkylamino(C_2-C_6)alkyl (meth)acrylamides.

Substituted (meth)acrylate and (meth)acrylamide monomers useful in the present invention are those with a dialkylamino group or dialkylaminoalkyl group in the alkyl radical. Examples of such substituted (meth)acrylates and (meth)acrylamides include, but are not limited to: dimethylaminoethyl methacrylate, dimethylaminoethyl acrylate, N,N-dimethylaminoethyl methacrylamide, N,N-dimethylaminopropyl methacrylamide, N,N-dimethylaminobutyl methacrylamide, N,N-di-ethylaminoethyl methacrylamide, N,N-diethylaminopropyl methacrylamide, N,N-diethylaminobutyl methacrylamide, N-(1,1-dimethyl-3-oxobutyl)acrylamide, N-(1,3-diphenyl-1-ethyl-3-oxobutyl) acrylamide, N-(1-methyl-1-phenyl-3-oxobutyl) methacrylamide, and 2-hydroxyethyl acrylamide, N-methacrylamide of aminoethyl ethylene urea, N-methacryloxy ethyl morpholine, N-maleimide of dimethylaminopropylamine and mixtures thereof.

Other substituted (meth)acrylate monomers useful in the present invention are silicon-containing monomers such as γ-propyl tri(C_1-C_6)alkoxysilyl(meth)acrylate, γ-propyl tri (C_1-C_6)alkylsilyl(meth)acrylate, γ-propyl di(C_1-C_6)alkoxy (C_1-C_6)alkylsilyl(meth)acrylate, γ-propyl di(C_1-C_6)alkyl (C_1-C_6)alkoxysilyl(meth)acrylate, vinyl tri(C_1-C_6) alkoxysilyl(meth)acrylate, vinyl di(C_1-C_6)alkoxy(C_1-C_6) alkylsilyl(meth)acrylate, vinyl(C_1-C_6)alkoxydi(C_1-C_6) alkylsilyl(meth)acrylate, vinyl tri(C_1-C_6)alkylsilyl(meth) acrylate, 2-propylsilsesquioxand(meth)acrylate and mixtures thereof.

The vinyl aromatic monomers useful as unsaturated monomers in the present invention include, but are not limited to: styrene ("STY"), hydroxystyrene, α-methylstyrene, vinyltoluene, p-methylstyrene, ethylvinylbenzene, vinylnaphthalene, vinylxylenes, and mixtures thereof. The vinylaromatic monomers also include their corresponding substituted counterparts, such as halogenated derivatives, i.e., containing one or more halogen groups, such as fluorine, chlorine or bromine; and nitro, cyano, (C_1-C_{10})alkoxy, halo(C_1-C_{10})alkyl, carb(C_1-C_{10}) alkoxy, carboxy, amino, (C_1-C_{10})alkylamino derivatives and the like.

The nitrogen-containing compounds and their thioanalogs useful as unsaturated monomers in the present invention include, but are not limited to: vinylpyridines such as 2-vinylpyridine or 4-vinylpyridine; lower alkyl(C_1-C_8) substituted N-vinyl pyridines such as 2-methyl-5-vinyl-pyridine, 2-ethyl-5-vinylpyridine, 3-methyl-5-vinylpyridine, 2,3-dimethyl-5-vinyl-pyridine, and 2-methyl-3-ethyl-5-vinylpyridine; methyl-substituted quinolines and isoquinolines; N-vinylcaprolactam; N-vinylbutyrolactam; N-vinylpyrrolidone; vinyl imidazole; N-vinyl carbazole; N-vinyl-succinimide; (meth)acrylonitrile; o-, m-, or p-aminostyrene; maleimide; N-vinyl-oxazolidone; N,N-dimethyl aminoethyl-vinyl-ether; ethyl-2-cyano acrylate; vinyl acetonitrile; N-vinylphthalimide; N-vinylpyrrolidones such as N-vinyl-thio-pyrrolidone, 3-methyl-1-vinyl-pyrrolidone, 4-methyl-1-vinyl-pyrrolidone, 5-methyl-1-vinyl-pyrrolidone, 3-ethyl-1-vinyl-pyrrolidone, 3-butyl-1-vinyl-pyrrolidone, 3,3-dimethyl-1-vinyl-pyrrolidone, 4,5-dimethyl-1-vinyl-pyrrolidone, 5,5-dimethyl-1-vinyl-pyrrolidone, 3,3,5-trimethyl-1-vinyl-pyrrolidone, 4-ethyl-1-vinyl-pyrrolidone, 5-methyl-5-ethyl-1-vinyl-pyrrolidone and 3,4,5-trimethyl-1-vinyl-pyrrolidone; vinyl pyrroles; vinyl anilines; and vinyl piperidines.

The substituted ethylene monomers useful as unsaturated monomers is in the present invention include, but are not limited to: vinyl acetate, vinyl formamide, vinyl chloride, vinyl fluoride, vinyl bromide, vinylidene chloride,

vinylidene fluoride, vinylidene bromide, tetrafluoroethylene, trifluoroethylene, trifluoromethyl vinyl acetate, vinyl ethers and itaconic anhydride.

Suitable cyclic olefin monomers useful in the present invention are (C_5-C_{10})cyclic olefins, such as cyclopentene, cyclopentadiene, dicylopentene, cyclohexene, cyclohexadiene, cycloheptene, cycloheptadiene, cyclooctene, cyclooctadiene, norbornene, maleic anhydride and the like. Such cyclic olefins also include spirocyclic olefin monomers such as spirocyclic norbornenyl monomers, spirocyclic cyclohexene monomers, spirocyclic cyclopentene monomers and mixtures thereof. Suitable substituted cyclic olefin monomers include, but are not limited to, cyclic olefins having one or more substituent groups selected from hydroxy, aryloxy, halo, (C_1-C_{12})alkyl, (C_1-C_{12})haloalkyl, (C_1-C_{12})hydroxyalkyl, (C_1-C_{12}) halohydroxyalkyl such as (CH_2)$_{n'}$C(CF_3)$_2$OH where n'=0 to 4, (C_1-C_{12})alkoxy, thio, amino, (C_1-C_6)alkylamino, (C_1-C_6)dialkylamino, (C_1-C_{12})alkylthio, carbo(C_1-C_{20}) alkoxy, carbo(C_1-C_{20})haloalkoxy, (C_1-C_{12})acyl, (C_1-C_6) alkylcarbonyl(C_1-C_6)alkyl, and the like. Particularly suitable substituted cyclic olefins include maleic anhydride and cyclic olefins containing one or more of hydroxy, aryloxy, (C_1-C_{12})alkyl, (C_1-C_{12})haloalkyl, (C_1-C_{12})hydroxyalkyl, (C_1-C_{12})halohydroxyalkyl, carbo(C_1-C_{20})alkoxy, and carbo(C_1-C_{20})haloalkoxy. It will be appreciated by those skilled in the art that the alkyl and alkoxy substituents may be optionally substituted, such as with halogen, hydroxyl, cyano, (C_1-C_6)alkoxyl, mercapto, (C_1-C_6)alkylthio, amino, a chromophore group and the like.

The polymeric particles of the present invention are typically cross-linked. Any amount of cross-linker is suitable for use in the present invention. Typically, the particles of the present invention contain at least 1% by weight, based on the total weight of the polymer, of cross-linker. Up to and including 100% cross-linking agent, based on the total weight of the polymer, may be effectively used in the particles of the present invention. It is preferred that the amount of cross-linker is from about 1% to about 80%, and more preferably from about 1% to about 60%.

Suitable cross-linkers useful in the present invention include di-, tri-, tetra-, or higher multi-functional ethylenically unsaturated monomers. Examples of cross-linkers useful in the present invention include, but are not limited to: trivinylbenzene, divinyltoluene, divinylpyridine, divinylnaphthalene and divinylxylene; and such as ethyleneglycol diacrylate, trimethylolpropane triacrylate, diethyleneglycol divinyl ether, trivinylcyclohexane, allyl methacrylate ("ALMA"), ethyleneglycol dimethacrylate ("EGDMA"), diethyleneglycol dimethacrylate ("DEGDMA"), propyleneglycol dimethacrylate, propyleneglycol diacrylate, trimethylolpropane trimethacrylate ("TMPTMA"), divinyl benzene ("DVB"), glycidyl methacrylate, 2,2-dimethylpropane 1,3 diacrylate, 1,3-butylene glycol diacrylate, 1,3-butylene glycol dimethacrylate, 1,4-butanediol diacrylate, diethylene glycol diacrylate, diethylene glycol dimethacrylate, 1,6-hexanediol diacrylate, 1,6-hexanediol dimethacrylate, tripropylene glycol diacrylate, triethylene glycol dimethacrylate, tetraethylene glycol diacrylate, polyethylene glycol 200 diacrylate, tetraethylene glycol dimethacrylate, polyethylene glycol dimethacrylate, ethoxylated bisphenol A diacrylate, ethoxylated bisphenol A dimethacrylate, polyethylene glycol 600 dimethacrylate, poly(butanediol)diacrylate, pentaerythritol triacrylate, trimethylolpropane triethoxy triacrylate, glyceryl propoxy triacrylate, pentaerythritol tetraacrylate, pentaerythritol tetramethacrylate, dipentaerythritol

monohydroxypentaacrylate, divinyl silane, trivinyl silane, dimethyl divinyl silane, divinyl methyl silane, methyl trivinyl silane, diphenyl divinyl silane, divinyl phenyl silane, trivinyl phenyl silane, divinyl methyl phenyl silane, tetravinyl silane, dimethyl vinyl disiloxane, poly(methyl vinyl siloxane), poly(vinyl hydro siloxane), poly(phenyl vinyl siloxane) and mixtures thereof.

The polymers of the present invention may further include as polymerized units one or more fluorinated monomers, one or more fluorinated cross-linkers or a mixture thereof. Such fluorinated components are particularly suitable for antireflective compoaitions useful with photoresists for imaging at 157 nm. Preferably, the fluorinated monomers or cross-linkers are highly fluorinated. Any monomer containing a fluoroalkyl group, such as trifluoromethyl, is particularly suitable. Suitable fluorinated monomers include, but are not limited to fluorinated (meth)acrylates and (meth) acrylamides such as fluoroalkyl(meth)acrylate such as fluoro(C_1-C_{20})alkyl(meth)acrylate, fluorocycloalkyl(meth) acrylate, fluoroalkylsulfoamidoethyl(meth)acrylate, fluoroalkylamidoethyl(meth)acrylate, fluoroalkyl(meth) acrylamide, fluoroalkylpropyl(meth)acrylate, fluoroalkylethyl poly(alkyleneoxide)(meth)acrylate, fluoroalkylsulfoethyl(meth)acrylate, αH,αH,ωH,ωH-perfluoroalkanediol di(meth)acrylate and β-substituted fluoroalkyl(meth)acrylate; fluorinated vinyl ethers such as fluoroalkylethyl vinyl ether and fluoroalkylethyl poly (ethyleneoxide)vinyl ether; fluorinatedalcohol vinyl ethers; fluorinated vinyl acetates; fluorinatedalkyl vinyl acetates such as trifluoromethyl vinyl acetate; fluorinated aromatics such as fluorostyrene, pentafluoro styrene and fluoroalkyl styrene; fluorinated hydroxyaromatics such as fluorinated hydroxystyrene; fluorinated ethylene such as vinylidene fluoride, trifluoroethylene and tetrafluoroethylene; fluorinated α-olefins; fluorinated dienes such as perfluorobutadiene and 1-fluoroalkylperfluorobutadiene, fluorinated heterocycles such as perfluoro-(2,2-dimethyl-1,3-dioxole) and perfluoro-(2-methylene-4-methyl-1,3-dioxolane). Preferred fluorainated monomers include 3-fluorostyrene, 4-fluorosytrene, perfluorooctylethyl(meth)acrylate, perfluorooctylethyl(meth)acrylate, octafluoropentyl(meth) acrylate, trifluoroethyl(meth)acrylate, tetrafluoropropyl (meth)acrylate, vinylidene fluoride, trifluoroethylene, tetrafluoroethylene, perfluoro-(2,2-dimethyl-1,3-dioxole) and perfluoro-(2-methylene-4-methyl-1,3-dioxolane).

It will be appreciated that oligomers may be used in preparing the present polymeric particles. Thus, for use with photoresists for imaging at sub-200 nm wavelength radiation, fluorinated oligomers may suitable be employed. Suitable fluorinated oligomers are disclosed in published PCT patent application WO 00/17712. Suitable oligomers include those prepared from the following monomer combinations: TFE/norbornene, TFE/nonbornene carboxylic acid, TFE/norbonene/nonbornene carboxylic acid, TFE/ nonbornene/acrylic acid, TFE/nonbornene/ethylene, TFE/ nonbornene/methacrylic acid, TFE/nonbornene/tert-butyl acrylate, TFE/nonbornene/tert-butyl acrylate/acrylic acid, TFE/nonbornene/tert-butyl acrylate/methacrylic acid, TFE/ nonbornene/vinyl acetate, TFE/nonbornene/vinyl alcohol, TFE/nonbornene/5-norbornene-2-carboxylic acid tert-butyl ester, TFE/1-adamantane-carboxylate vinyl ester, TFE/ adamantanemethylvinyl ether and TFE/ norbornanemethylvinyl ether.

It is further preferred that the polymer particles of the present invention contain functionality that allows the particles to be further cross-linked with each other, such as to provide a cross-linked coating. Suitable functional groups

include, but are not limited to, hydroxyl groups, carboxyl groups, amines and the like. Such functionality may reside in the polymer backbone or pendant groups. Thus, it is preferred that the polymeric particles of the present invention include as polymerized units one or more monomers containing hydroxyl groups, carboxyl groups, amines and the like. Suitable functional group containing monomers include, but are no limited to, (meth)acrylamide, hydroxyalkyl(meth)arylates, alkylamino(C_2–C_6)alkyl(meth) arylates, alkylamino(C_2–C_6)alkyl(meth)arylamides and the like.

Particularly useful hydroxyalkyl(meth)acrylate monomers are those with one or more hydroxyl groups in the alkyl radical, especially those where the hydroxyl group is found at the β-position (2-position) in the alkyl radical. Hydroxyalkyl(meth)acrylate monomers in which the substituted alkyl group is a (C_2–C_6)alkyl, branched or unbranched, are preferred. Suitable hydroxyalkyl(meth)acrylate monomers include, but are not limited to: 2-hydroxyethyl methacrylate ("HEMA"), 2-hydroxyethyl acrylate ("HEA"), 2-hydroxypropyl methacrylate, 1-methyl-2-hydroxyethyl methacrylate, 2-hydroxy-propyl acrylate, 1-methyl-2-hydroxyethyl acrylate, 2-hydroxybutyl methacrylate, 2-hydroxybutyl acrylate and mixtures thereof. The preferred hydroxyalkyl(meth)acrylate monomers are HEMA, 1-methyl-2-hydroxyethyl methacrylate, 2-hydroxypropyl methacrylate and mixtures thereof. A mixture of the latter two monomers is commonly referred to as "hydroxypropyl methacrylate" or HPMA.

The polymeric particles useful in the present invention may be prepared by any of a variety of methods, such as solution polymerization, emulsion polymerization, dispersion polymerization and the like. For example, the nanoparticles or nanogel particles may be prepared by solution of emulsion polymerization. The core-shell polymer particles are typically prepared by emulsion or dispersion polymerization. It is preferred that the polymers of the present invention are prepared using anionic polymerization or free radical polymerization techniques. It is also preferred that the polymers useful in the present invention are not prepared by step-growth polymerization processes.

Polymeric particles prepared by solution polymerization are generally prepared by first charging a solvent heel or alternatively a mixture of solvent and some portion of the monomer mixture to a reaction vessel equipped with a stirrer, a thermometer and a reflux condenser. The monomer mixture is typically composed of monomer, initiator and chain transfer agent, as appropriate. The solvent or solvent/ monomer mixture heel is heated with stirring under a nitrogen blanket to a temperature from about 55° C. to about 125° C. After the heel charge has reached a temperature sufficient to initiate polymerization, the monomer mixture or balance of the monomer mixture is charged to the reaction vessel over a period of 15 minutes to 4 hours while maintaining the reaction at the desired reaction temperature. After completing the monomer mixture addition, a series of additional aliquots of initiator in solvent are charged to the reaction. Typically, the initiator is charged to the reaction and followed by a hold period to allow for reaction to occur before adding the next initiator amount. Typically three initiator additions are used. After the final initiator amount is added the batch is held for 30 minutes to 4 hours to fully decompose all initiator and drive the reaction to completeness. An alternative method is to first charge both solvent and a portion of the monomer mixture to the reaction vessel.

Polymeric particles prepared by emulsion polymerization are generally prepared by first charging water and some portion of the monomer emulsion to a reaction vessel equipped with a stirrer, a thermometer and a reflux condenser. Typically, the monomer emulsion is composed of monomer, surfactant, initiator and chain transfer agent, as appropriate. The initial charge of monomer emulsion is heated with stirring under a nitrogen blanket to a temperature of from about 55° C. to about 125° C. After the seed charge has reached a temperature sufficient to initiate polymerization, the monomer emulsion or balance of the monomer emulsion is charged to the reaction vessel over a period of 15 minutes to 4 hours while maintaining the reaction at the desired reaction temperature. After completing the monomer emulsion addition, a series of additional aliquots of initiator in water are charged to the reaction. Typically the initiator is charged to the reaction and followed by a hold period to allow for reaction to occur before adding the next initiator amount. Typically three initiator additions are used. After the final initiator amount is added, the batch is held for 30 minutes to 4 hours to fully decompose all initiator and drive the reaction to completeness.

In the alternative, the emulsion polymerization may be carried out in a batch process. In such a batch process, the emulsion polymers are prepared by charging water, monomer, surfactant, initiator and chain transfer agent, as appropriate, to a reaction vessel with stirring under a nitrogen blanket. The monomer emulsion is heated to a temperature of from about 55° C. to about 125° C. to carry out the polymerization. After 30 minutes to 4 hours at this temperature, a series of additional aliquots of initiator are charged to the reaction vessel. Typically the initiator is charged to the reaction vessel followed by a hold period to allow for reaction to occur before adding the next amount of initiator. Typically three initiator additions are used. After the final initiator amount is added, the batch is held for 30 minutes to 4 hours to fully decompose all initiator and drive the reaction to completeness.

Core-shell polymeric particles are particles have a core material surrounded by one or more discrete polymer shells. "Discrete" is understood to mean separate and distinct. "Core material" includes a single material or a mixture of materials. The term "shell" refers to a discrete layer completely encasing the core material and generally immiscible in the core material. Such core-shell particles are typically prepared by (a) providing a first emulsion comprising a core material in an aqueous phase, a second emulsion comprising polymer seed particles, one or more monomers and optionally one or more cross-linking agents; (b) combining the first emulsion, the second emulsion, one or more monomers and optionally one or more cross-linking agents; (c) forming discrete domains in the aqueous phase, wherein the domains include the core material, one or more monomers and optionally one or more cross-linking agents; (d) polymerizing the one or more monomers and optional cross-linking agents to form a plurality of polymer particles, each particle including a discrete polymer shell encasing the core material. Multiple shells may be provided by swelling the particle from step (d) with one or more additional monomers and polymerizing the additional monomers. It will be appreciated by those skilled in the art that the one or more monomers or the one or more cross-linking agents in step (a) may be added to the first emulsion, the second emulsion, to both emulsions, or to the combined first and second emulsions. The preparation of such core-shell particles is disclosed in European Patent Application EP 915 147 (Clikeman et al.) and U.S. Pat. No. 6,037,058 (Clikeman et al.).

In such core-shell particles, a wide variety of materials may be used as the core material. Suitable core materials

include, but are not limited to, cross-linking catalysts such as photoacid generators, dyes, solvent, and the like. It will also be appreciated that the core material, such as a solvent, may be removed from the particle, to provide a hollow-sphere particle.

The particles of the present invention may be surface modified after polymerization, such as by reacting the particles with one or more other components. Such surface modification may be advantageous in certain systems where surfactant functionality, cross-linkable functionality or other functionality on the polymer surface is desired.

The particles of the present invention may be isolated, typically in powder form but may also be gels or solutions. The isolated particles may then be taken up in any of a variety of solvents including water, or may be used as is. If the particles are to be taken up in water, it may be desirable to use a surfactant or wetting agent and/or surface modify the particles to provide water solubility or dispersability.

One of the advantages of the present antireflective compositions is that the size of the polymer particles can be carefully tailored. Suitable polymer particles are those having a mean particle size up to about 1000 nm, such as in the range of about 1 to about 1000 nm. It is preferred that the mean particle size is in the range of about 1 to about 200 nm, more preferably from about 1 about 50 nm, still more preferably from about 1 nm to about 20 nm, and most preferably from about 1 to about 10 nm. Solution polymer particles typically have a weight average molecular weight in the range of 10,000 to 1,000,000, preferably in the range of 20,000 to 500,000 and more preferably in the range of 20,000 to 100,000. The polydispersity of these solution polymers is in the range 1 to 20 and more preferably in the range of 1.001 to 15 and most preferably in the range of 1.001 to 10. The emulsion polymer particles typically have a weight average molecular weight in the range of 1000 to 10,000,000, preferably 100,000 to 5,000,000, and more preferably 100,000 to 1,000,000. The polydispersity of these emulsion polymer particles is in the range 1.0001 to 10, more preferably 1.001 to 5, and most preferably 1.001 to 2.5. Polydispersities of about 1.3 to 1.0 can be achieved for core-shell particles. The term "polydispersity" is known in the art as an indicator of the breadth of domain size (or particle size) distribution. Polydispersity as used herein is calculated by dividing the weight average size by the number average size. A polydispersity of one (1) refers to particles that are monodisperse. Thus, the present invention provides an antireflective composition including a plurality of polymer particles wherein each particle in the plurality has a mean particle size of up to about 1000 nm.

The antireflective compositions of the present invention preferably include a plurality of cross-linked polymer particles having one or more chromophores, one or more cross-linking agents and a cross-linking catalyst. Any cross-linking agent that cross-links the polymeric particles to form a cured antireflective coating layer is suitable. Thus, any of the cross-linking agents disclosed above may also be used in the antireflective compositions. It is preferred that the cross-linking agents for use in the antireflective compositions are glycolsyl ureas, such as those sold under the POWDER-LINK trademark (available from Cytek Technology Corp), melamines and the like.

The cross-linking catalysts useful in the present invention are typically acids, photoacid generators, photobase generators or mixtures of acids and photoacid generators. It is preferred that the catalyst is an acid, photoacid generator or mixture thereof. Suitable acids include organic acids such as sulfonic acids. Aromatic sulfonic acids such as phenylsul-

fonic acid and para-toluenesulfonic acid are particularly suitable. More than one cross-linking catalyst may be advantageously used in the present invention.

The photoacid generators useful in the present invention are any compounds which liberate acid upon exposure to light, typically at a wavelength of about 320 to 420 nanometers, however other wavelengths may be suitable. Suitable photoacid generators include halogenated triazines, onium salts, sulfonated esters, halogenated sulfonyloxy dicarboximides, diazodisulfones, α-cyanooxyaminesulfonates, imidesulfonates, ketodiazosulfones, sulfonyldiazoesters, 1,2-di(arylsulfonyl) hydrazines and the like.

Particularly useful halogenated triazines include halomethyl-s-triazines. Suitable halogenated triazines include for example, 2-[1-(3,4-benzodioxolyl)]-4,6-bis (trichloromethyl)-1,2,5-triazine, 2-[1-(2,3-benzodioxolyl)]-4,6-bis(trichloromethyl)-1,3,5-triazine, 2-[1-(3,4-benzodioxolyl)]-4,6-bis(tribromomethyl)-1,3,5-triazine, 2-[1-(2,3-benzodioxolyl)]-4,6-bis(tribrommethyl)-1,3,5-triazine, 2-(2-furfylethylidene)-4,6-bis(trichloromethyl)-1, 3,5-triazine, 2-[2-(5-methylfuryl)ethylidene]-4,6-bis (trichloromethyl)-1,3,5-triazine, 2-[2-(4-methylfuryl) ethylidene]-4,6-bis(trichloromethyl)-1,3,5-triazine, 2-[2-(3-methylfuryl)ethylidene]-4,6-bis-(trichloromethyl)-1,3,5-triazine, 2-[2-(4,5-dimethylfuryl)ethylidene]-4,6-bis (trichloromethyl)-1,3,5-triazine, 2-[2-(5-methoxyfuryl) ethylidene]-4,6-bis(trichloromethyl)-1,3,5-triazine, 2-[2-(4-methoxyfuryl)ethylidene]-4,6-bis(trichloromethyl)-1,3,5-triazine, 2-[2-(3-methoxyfuryl)ethylidene]-4,6-bis (trichloromethyl)-1,3,5-triazine, 2-[2-(4,5-dimethoxy-furyl) ethylidene]-4,6-bis(trichloromethyl)-1,3,5-triazine, 2-(2-furfylethylidene)-4,6-bis(tribromomethyl)-1,3,5-triazine, 2-[2-(5-methylfuryl)ethylidene]-4,6-bis(tribromomethyl)-1, 3,5-triazine, 2-[2-(4-methylfuryl)-ethylidene]-4,6-bis (tribromomethyl)-1,3,5-triazine, 2-[2-(3-methylfuryl) ethylidene]-4,6-bis(tribromomethyl)-1,3,5-triazine, 2-[2-(4, 5-dimethoxy-furyl)ethylidene]-4,6-bis(tribromomethyl)-1, 3,5-triazine, 2-[2-(5-methoxyfuryl)ethylidene]-4,6-bis (tribromomethyl)-1,3,5-triazine, 2-[2-(4-methoxylfuryl) ethylidene]-4,6-bis(tribromomethyl)-1,3,5-triazine, 2-[2-(3-methoxyfuryl)ethylidene]-4,6-bis(tribromomethyl)-1,3,5-triazine, 2-[2-(4,5-dimethoxyfuryl)ethylidene]-4,6-bis (tribromomethyl)-1,3,5-triazine, 2,4,6-tris-(trichloromethyl)-1,3,5-triazine, 2,4,6-tris-(tribromomethyl)-1,3,5-triazine, 2-phenyl-4,6-bis (trichloromethyl)-1,3,5-triazine, 2-phenyl-4,6-bis (tribromomethyl)-1,3,5-triazine, 2-(4-methoxyphenyl)-4,6-bis(trichloromethyl)-1,3,5-triazine, 2-(4-methoxyphenyl)-4, 6-bis(tribromomethyl)-1,3,5-triazine, 2-(1-naphthyl)-4,6-bis (trichloromethyl)-1,3,5-triazine, 2-(1-naphthyl)-4,6-bis (tribromomethyl)-1,3,5-triazine, 2-(4-methoxy-1-naphthyl)-4,6-bis(trichloromethyl)-1,3,5-triazine, 2-(4-methoxy-1-naphthyl)-4,6-bis(tribromomethyl)-1,3,5-triazine, 2-(4-chlorophenyl)-4,6-bis(tribromomethyl)-1,3,5-triazine, 2-styryl-4,6-bis(trichloromethyl)-1,3,5-triazine, 2-styryl-4, 6-bis(tribromomethyl)-1,3,5-triazine, 2-(4-methoxystyryl)-4,6-bis(trichloromethyl)-1,3,5-triazine, 2-(4-methoxy styryl)-4,6-bis(tribromomethyl)-1,3,5-triazine, 2-(3,4,5-trimethoxystyryl)-4,6-bis(trichloromethyl)-1,3,5-triazine, 2-(3,4,5-trimethoxystyryl)-4,6-bis(tribromomethyl)-1,3,5-triazine, 2-(3-chloro-1-phenyl)-4,6-bis(trichloromethyl)-1, 3,5-triazine, 2-(3-chlorophenyl)-4,6-bis(tribromomethyl)-1, 3,5-triazine and the like. Other triazine type photoacid generators useful in the present invention are disclosed in U.S. Pat. No. 5,366,846, herein incorporated by reference.

The s-triazine compounds are condensation reaction products of certain methyl-halomethyl-s-triazines and certain

aldehydes or aldehyde derivatives. Such s-triazine compounds may be prepared according to the procedures disclosed in U.S. Pat. No. 3,954,475 and Wakabayashi et al., *Bulletin of the Chemical Society of Japan*, 42, 2924–30 (1969).

Onium salts with weakly nucleophilic anions are suitable for use as photoacid generators in the present invention. Examples of such anions are the halogen complex anions of divalent to heptavalent metals or non-metals, for example, antimony, tin, iron, bismuth, aluminum, gallium, indium, titanium, zirconium, scandium, chromium, hafnium, copper, boron, phosphorus and arsenic. Examples of suitable onium salts include, but are not limited to: diaryl-diazonium salts and onium salts of group VA and B, IIA and B and I of the Periodic Table, for example, halonium salts such as iodonium salts, quaternary ammonium, phosphonium and arsonium salts, aromatic sulfonium salts and sulfoxonium salts or selenium salts. Examples of suitable onium salts are disclosed in U.S. Pat. Nos. 4,442,197; 4,603,101; and 4,624,912, all incorporated herein by reference.

The sulfonated esters useful as photoacid generators in the present invention include sulfonyloxy ketones. Suitable sulfonated esters include, but are not limited to: benzoin tosylate, t-butylphenyl alpha-(p-toluenesulfonyloxy)-acetate, and t-butyl alpha-(p-toluenesulfonyloxy)-acetate. Such sulfonated esters are disclosed in the *Journal of Photopolymer Science and Technology*, vol. 4, No. 3,337–340 (1991), incorporated herein by reference.

Suitable halogenated sulfonyloxy dicarboximides useful as photoacid generators in the present invention include, but are not limited to: 1(((trifluoromethyl)sulfonyl)oxy)-1H-pyrrole-2,5-dione; N-((perfluorooctanesulfonyl)oxy)-5-norbornene-2,3-dicarboximide; 1-(((trifluoromethyl)sulfonyl)oxy)-2,5-pyrrolidinedione; 3a,4,7,7a-tetrahydro-2-(((trifluoromethyl)sulfonyl)oxy)-4,7-methano-1H-isoindole-1,3(2H)-dione; 2-(((trifluoromethyl)sulfonyl)oxy)-1H-benz(f)isoindole-1,3(2H)-dione; 3,4-dimethyl-1-(((trifluoromethyl)sulfonyl)oxy)-1H-pyrrole-2,5-dione; 2-(((trifluoromethyl)sulfonyl)oxy)-1II-isoindole-1,3(2II)-dione; 2-(((trifluoromethyl)sulfonyl)oxy)-1H-benz(de) isoquinoline-1,3(2H)-dione; 4,5,6,7-tetrahydro-2-(((trifluoromethyl)sulfonyl)oxy)-1H-isoindole-1,3(2H)-dione; 3a,4,7,7a-tetrahydro-2-(((trifluoromethyl)sulfonyl)oxy)-4,7-epoxy-1H-isoindole-1,3(2H)-dione; 2,6-bis-(((trifluoromethyl)sulfonyl)oxy)-benzo(1,2-c:4,5-c') dipyrrole-1,3,5,7(2H,6H)-tetrone; hexahydro-2,6-bis-(((trifluoromethyl)sulfonyl)oxy)-4,9-methano-1H-pyrrolo (4,4-g)isoquinoline-1,3,5,7(2H,3aH,6H)-tetrone; 1,8,8-trimethyl-3-(((trifluoromethyl)sulfonyl)oxy)-3-azabicyclo (3.2.1)octane-2,4-dione; 4,7-dihydro-2--(((trifluoromethyl) sulfonyl)oxy)-4,7-epoxy-1H-isoindole-1,3(2H)-dione; 3-(1-naphthalenyl)-4-phenyl-1--(((trifluoromethyl)sulfonyl) oxy)-1H-pyrrole-2,5-dione; 3,4-diphenyl-1--(((trifluoromethyl)sulfonyl)oxy)-1H-pyrrole-2,5-dione; 5,5'-(2,2,2-trifluoro-1-(trifluoromethyl)ethylidene)bis(2-(((trifluoromethyl)sulfonyl)oxy)-1II-isoindole-1,3(2II)-dione; tetrahydro-4-(((trifluoromethyl)sulfonyl)oxy)-2,6-methano-2H-oxireno(f)isoindole-3,5(1aH,4H)-dione; 5,5'-oxybis-2-(((trifluoromethyl)sulfonyl)oxy)-1H-isoindole-1,3 (2H)-dione; 4-methyl-2-(((trifluoromethyl)sulfonyl)oxy)-1H-isoindole-1,3(2H)-dione; 3,3,4,4-tetramethyl-1-(((trifluoromethyl)sulfonyl)oxy)-2,5-pyrrolidinedione and mixtures thereof. It is preferred that the halogenated sulfonyloxy dicarboximides comprise one or more of 1(((trifluoromethyl)sulfonyl)oxy)-1H-pyrrole-2,5-dione; N-((perfluorooctanesulfonyl)oxy)-5-norbornene-2,3-dicarboximide; and 1-(((trifluoromethyl)sulfonyl)oxy)-2,5-

pyrrolidinedione, and more preferably N-((perfluorooctanesulfonyl)oxy)-5-norbornene-2,3-dicarboximide.

Suitable diazodisulfones include those of the formula R^1—SO_2—$C(=N_2)$—SO_2—R^2, wherein R1 and R2 are independently selected from a monovalent cyclic group substituted on the cyclic nucleus by an acid-dissociable group such as tert-butoxycarbonyl and acetal groups, or phenyl or substituted phenyl. Suitable R^1 and R^2 groups include tert-butoxycarbonyl phenyl, (2-tetrahydropyranyl) oxy phenyl, (2-tetrahydropyranyl)oxycarbonyl phenyl, tert-butoxycarbonylmethyloxy phenyl, (2-tetrahydropyranyl) oxycyclohexyl, (2-tetrahydropyranyl)oxy-10-bornyl, (1-ethoxyethoxy)cyclohexyl and (1-ethoxyethoxy)-10-bornyl. Certain diazomethanesulfones are disclosed in U.S. Pat. No. 5,945,517.

The cross-linking catalysts are typically added to photoresist compositions in an amount sufficient to catalyze the curing of the polymeric particles of the present invention with one or more cross-linking agents. When the cross-linking catalyst is a photoacid generator, the amount is typically in the range of 0.1 to 15 percent by weight, based on the weight of the resin, and preferably 1 to 10 percent by weight. It will be appreciated by those skilled in that art that more than one photoacid generators may be used advantageously in the photoresist compositions of the present invention.

Optional additives that may be used in the photoresist compositions of the present invention include, but are not limited to: anti-striation agents, plasticizers, speed enhancers, fillers, dyes, film forming agents, cross-linking agents and the like. Such optional additives will be present in relatively minor concentrations in a photoresist composition except for fillers and dyes which may be used in relatively large concentrations, e.g. in amounts of from about 5 to 30 percent by weight, based on the total weight of the composition's dry components.

In general, the polymer particles of the present invention have excellent film forming properties, and thus additional film forming agents are not required. For example, (meth) acrylate containing polymer particles, whether nanoparticles, nanogels or core-shell particles have good film forming properties and good adhesiveness to the substrate. However, such film forming agents may be advantageous in certain applications or with certain polymer particles.

The antireflective compositions of the present invention may be readily prepared by those skilled in the art. For example, an antireflective composition of the invention can be prepared by dissolving, suspending or dispersing the desired components in one or more suitable solvents. Such suitable solvents include, but are not limited to: ketone solvents such as acetone, methyl ethyl ketone, cyclohexanone, methyl isoamyl ketone and 2-heptanone; polyhydric alcohols and derivatives thereof such as ethyleneglycol, ethyleneglycol monoacetate, diethyleneglycol, diethyleneglycol monoacetate, propyleneglycol, propyleneglycol monoacetate, dipropyleneglycol and dipropyleneglycol monoacetate as well as monomethyl, monoethyl, monopropyl, monobutyl and monophenyl ethers thereof, cyclic ether solvents such as dioxane; ester solvents such as methyl lactate, ethyl lactate, methyl acetate, ethyl acetate, butyl acetate, methyl pyruvate, ethyl pyruvate, methyl methoxypropionate and ethyl ethoxypropionate; and amide solvents such as N,N-dimethyl formamide, N,N-dimethyl acetamide, N-methyl-2-pyrrolidone, 3-ethoxyethyl propionate, 2-heptanone, γ-butyrolactone, and mixtures thereof.

Typically, the solids content of the present antireflective compositions varies from about 5 to about 35 percent by weight, based on the total weight of the composition, but may be higher or lower. The resin binder should be present in amounts sufficient to provide a film coating layer and absorption and/or attenuation of the radiation used to image the photoresist.

Such antireflective compositions may be applied to a substrate by any known means, such as spinning, dipping, roller coating and the like. When the compositions are applied by spin coating, the solids content of the coating solution can be adjusted to provide a desired film thickness based upon the specific spinning equipment utilized, the viscosity of the solution, the speed of the spinner and the amount of time allowed for spinning.

Antireflective compositions including the polymeric particles of the present invention are useful in all applications where antireflective compositions are typically used. The antireflective compositions of the present invention may be used as TARCs or BARCs. For example, the compositions may be applied over silicon wafers or silicon wafers coated with silicon dioxide for the production of microprocessors and other integrated circuit components. Aluminum-aluminum oxide, gallium arsenide, ceramic, quartz, copper, glass and the like are also suitably employed as substrates for the antireflective compsitions of the invention. When the present compositions are used as TARCs, they may be applied over a wide variety of photoresist compositions.

Once the antireflective composition is coated on a substrate surface, it is dried by heating to remove any solvent. It is preferably dried until the coating is tack free. An advantage of the present invention is that the viscosity of the present antireflective compositions is lower than conventional photoresists providing more application process control and reduced defects during imaging. Also, films of the present photoresist compositions have greater film uniformity than those of conventional antireflective compositions.

After the antireflective composition is dried, it is optionally heated or subjected to radiation to form a cured antireflective coating layer. When the antireflective composition contains one or more cross-linking agents, it is preferred that the composition is cured. Such curing helps to reduce intermixing with a previously applied or subsequently applied photoresist. An advantage of the present compositions is that the amount of cross-linking agent used in the antireflective compositions can be eliminated or reduced, as compared to conventional antireflective compositions. While not wishing to be bound by theory, it is believed that such reduction in th eamount of cross-linker is due to the polymeric particles already possessing some degree of cross-linking.

When the present antireflective compositions are used as BARCs, a photoresist is subsequently applied after curing. The photoresist is imaged through a mask in a conventional manner.

The antireflective compositions of the present invention are suited for use with photoresists activated by a short exposure wavelength, particularly a sub-300 nm, such as UV, and more preferably a sub-200 nm exposure wavelength. Particularly preferred wavelengths include 248, 193, 157 nm and 11–15 nm. However, the antireflective compositions of the present invention may also be used with photoresists that are imaged at higher wavelengths, such as, but not limited to, visible, e-beam and x-ray.

Following exposure, the photoresist is optionally baked, such as at temperatures ranging from about 70° C. to 160° C. Thereafter, the photoresist is developed. The exposed resist film is rendered positive working by employing a polar developer, preferably an aqueous based developer, such as quarternary ammonium hydroxide solutions, such as tetra-alkyl ammonium hydroxide, preferably a 0.26 N tetramethy-lammonium hydroxide; various amine solutions, such as ethylamine, n-propylamine, diethylamine, triethylamine or methyl diethylamine; alcohol amines, such as diethanolamine, triethanolamine; cyclic amines, such as pyrrole, pyridine, and the like. One skilled in the art will appreciate which development procedures should be used for a given system.

After development of the photoresist coating, the developed substrate may be selectively processed on those areas bared of resist, for example, by chemically etching or plating substrate areas bared of resist in accordance with procedures known in the art. For the manufacture of microelectronic substrates, e.g. the manufacture of silicon dioxide wafers, suitable etchants include, but are not limited to, a gas etchant, such as a chlorine- or fluorine-based etchant, such as Cl_2 or CF_4/CHF_3 etchant applied as a plasma stream. After such processing, the resist may be removed from the processed substrate using any stripping procedures known in the art.

An advantage of the present antireflective compositions is that the compositions may be carefully controlled so as to provide etch rates equal to or faster than the photoresist employed. Such etch rates may be controlled without sacrificing the radiation absorbing or attenuating properties of the polymeric particles.

It will be appreciated by those skilled in the art that the present antireflective compositions may be combined with one or more conventional antireflective compositions to provide a wide range of desired properties.

The following examples are intended to illustrate further various aspects of the present invention, but are not intended to limit the scope of the invention in any aspect.

EXAMPLE 1

A plurality of nongel polymer particles were prepared by free radical solution polymerization according to the procedure in U.S. Pat. No. 5,863,996 (Graham). The polymer compositions are reported in the Table. All amounts are % by weight, based on the total weight of the monomers. The mole ratios of ANTMA/HEMA/MMA were 20/30/50.

Sample	ANTMA	HEMA	MMA	TMPTMA
1	37.7	24.2	31.1	7
2	38.5	24.8	31.7	5

EXAMPLE 2

An antireflective composition was prepared by combining the polymer of Sample 1 from Example 1 (15%), a glycosyl urea cross-linking agent (5%) (POWDERLINK® 1174), para-toluene sulfonic acid (1%), di-(para-tert-butylphenyl) iodonium camphorsulfonate (1%) and propylene glycol monomethyl ether (to make 100%). All percentages were by weight, based on the total weight of the composition. Once combined, the compositions was rolled on a roller mill until thoroughly mixed and then filtered through a 0.2 μm filter.

EXAMPLE 3

A layer of the antireflective composition from Example 2 was coated on a substrate to a thickness of 600 Å and then

baked at 185° C. for 60 seconds. A photoresist, UV6 (available from Shipley Company, Marlborough, Mass.) was then applied to the antireflective coating layer. The thickness of the photoresist was 6000 Å. The photoresist was then baked at 130° C. for 60 seconds. The photoresist was hen exposed at 248 nm through a mask to provide 220 nm features. Following exposure, the photoresist was baked at 130° C. for 90 seconds and then developed using 0.26 N tetramethylammonium hydroxide. The results are shown in FIGS. 2 and 3. FIG. 2 is a scanning electron micrograph ("SEM") of dense 220 nm features and FIG. 3 is a SEM of an isolated 220 nm feature. These figures show no standing wave effects. These data clearly show that the cross-linked polymeric particles of the present invention are effective as antireflective compositions.

EXAMPLE 4

The composition of Example 2 was coated over a patterned 1900 Å silicon dioxide substrate. Very good planarizing results were obtained. The results are shown in FIG. 4, which is a SEM showing that the antireflective compositions of the present invention are substantially planarizing.

What is claimed is:

1. An antireflective composition comprising a plurality of cross-linked polymeric particles having one or more chromophores.

2. The composition of claim 1 wherein the chromophore comprises an aromatic or substituted aromatic moiety.

3. The composition of claim 2 wherein the chromophore is selected from phenyl, substituted phenyl, naphthyl, substituted naphthyl, anthracenyl, substituted anthracenyl, phenanthrenyl or substituted phenanthrenyl.

4. The composition of claim 1 wherein the chromophore is a monomer containing one or more (C_4-C_{20})alkyl groups.

5. The composition of claim 1 further comprising one or more cross-linking agents.

6. The composition of claim 5 wherein the cross-linking agent is selected from glycosyl urea or melamine.

7. The composition of claim 5 further comprising one or more cross-linking catalysts.

8. The composition of claim 7 wherein the cross-linking catalyst is an acid.

9. The composition of claim 1 wherein the polymeric particle has a mean particle size of from about 1 to about 1000 nm.

10. The composition of claim 9 wherein the polymeric particle has a mean particle size of from about 1 to about 200 nm.

11. The composition of claim 9 wherein the polymeric particle has a mean particle size of from about 1 about 50 nm.

12. The composition of claim 1 wherein the polymeric particle has a polydispersity of from 1.001 to 15.

13. The composition of claim 1 wherein the polymeric particle comprises as polymerized units one or more fluorinated monomers.

14. A method for forming an antireflective coating layer comprising the step of disposing on a substrate a composition comprising a plurality of cross-linked polymeric particles having one or more chromophores.

15. The method of claim 14 wherein the chromophore comprises an aromatic moiety, substituted aromatic moiety or one or more (C_4-C_{20})alkyl groups.

16. The method of claim 15 wherein the chromophore is selected from phenyl, substituted phenyl, naphthyl, substituted naphthyl, anthracenyl, substituted anthracenyl, phenanthrenyl or substituted phenanthrenyl.

17. The method of claim 14 wherein the antireflective composition further comprises one or more cross-linking agents.

18. The method of claim 14 wherein the polymeric particle has a mean particle size of from about 1 to about 1000 nm.

19. The method of claim 14 wherein the polymeric particle has a polydispersity of from 1.001 to 15.

20. A method for forming a photoresist relief image, comprising the steps of applying a coating layer of an antireflective composition comprising a plurality of cross-linked polymeric particles having one or more chromophores; applying a photoresist coating layer to the surface of the antireflective coating layer; exposing the photoresist coating layer to patterned activating radiation; and developing the exposed photoresist coating layer to provide a photoresist relief image.

21. An antireflective composition comprising a plurality of cross-linked core-shell polymeric particles having one or more chromophores, wherein an absorbing component is contained within the polymeric particle.

22. A method for manufacturing an electronic device comprising the steps of disposing on the surface of a substrate a coating layer of an antireflective composition comprising a plurality of cross-linked polymer particles having one or more chromophores; disposing on the surface of the antireflective coating layer a coating layer of a photoresist composition; exposing the photoresist coating layer to patterned activating radiation; and developing the exposed photoresist coating layer to provide a photoresist relief image.

23. The method of claim 22 wherein the chromophore comprises an aromatic moiety, substituted aromatic moiety or one or more (C_4-C_{20})alkyl groups.

24. The method of claim 23 wherein the chromophore is selected from phenyl, substituted phenyl, naphthyl, substituted naphthyl, anthracenyl, substituted anthracenyl, phenanthrenyl or substituted phenanthrenyl.

25. The method of claim 22 wherein the antireflective composition further comprises one or more cross-linking agents.

26. The method of claim 22 wherein the polymeric particle has a mean particle size of from about 1 to about 1000 nm.

27. The method of claim 22 wherein the polymeric particle has a polydispersity of from 1.001 to 15.

28. The method of claim 22 wherein the polymeric particle comprises as polymerized units one or more fluorinated monomers.

*   *   *   *   *